Preparation of Silicon Carbide–Silicon Nitride Fibers by the Controlled Pyrolysis of Polycarbosilazane Precursors

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Synopsis

Experiments to produce polycarbosilazane resin and high-strength silicon carbide–silicon nitride ($Si_xN_yC_z$) fibers as well as resin/fiber characteristics are reported. Polycarbosilazane resin was drawn into fibers from the melt and subsequently treated and pyrolyzed into $Si_xN_yC_z$ fibers. These materials are characterized by high tensile modulus (29×10^6 psi for 0.4-mil diameter) and high electrical resistivity (6.9×10^8 Ω·cm for 0.6-mil diameter).

INTRODUCTION

Recent efforts to develop new reinforcement fibers for use in composite materials have been prompted by the need for higher performance and decreased weight in parts used to construct aircraft and missiles as well as to reduce costs.[1]

Carbon fibers are widely used to construct fiber-reinforced composite materials. However, the fiber's high electrical conductivity has led to concern about safety during manufacturing, application, and disposal. This realization led to the initiation of a high-strength fiber development program in this laboratory to find reinforcement fibers whose physical properties are comparable to carbon but with lower electrical conductivity. Silicon carbide–silicon nitride ($Si_xN_yC_z$) fibers have been suggested as a potential candidate.[2]

The preparation of $Si_xN_yC_z$ fibers by the pyrolysis of polycarbosilazane resin has been reported by Verbeek.[3] In one example, polycarbosilazane precursor fibers, prepared by heating tris(N-methylamino)methylsilane for 3 h at 520°C, were pyrolyzed at 1200–1500°C in an inert atmosphere to yield silicon carbide–silicon nitride fibers. The black shiny, amorphous fiber had high tensile strength (188, 500 psi) and tensile modulus (29×10^6 psi). However, no mention was made of the fiber's electrical properties.

Polycarbosilazanes prepared from various monomers have been described in the literature.[4-6] The pyrolysis of these potential precursor materials may lead to the development of new $Si_xN_yC_z$ fibers with excellent physical and electrical resistivity properties.

This paper describes the preparation of $Si_xN_yC_z$ fibers by pyrolysis of polysilazanes prepared from tris(N-methylamino)methylsilane using a technique

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based on a method described by Verbeek.[3] In addition, the effects of reaction time and temperature on the molecular weight, the relationship of tensile rupture modulus to fiber diameter, and electrical resistivity properties were examined.

EXPERIMENTAL

Synthesis of Tris(N-Methylamino)Methylsilane

Into a 31 three-necked flask fitted with nitrogen inlet, condenser, and dropping funnel, was added 1500 mL of dry petroleum ether. The temperature was set at $-30°C$ and liquefied monomethylamine (150 g, 5 mol) was added to the reaction vessel. While stirring and maintaining a dry nitrogen atmosphere, methyltrichlorosilane (75 g, 0.5 mol) was added dropwise. The reaction vessel was then equipped with a Friedrichs condenser fitted with a drying tube and the other two necks sealed with glass stoppers. The entire reaction apparatus was transferred to a hood and the reaction mixture heated at $40°C$ for 1 h. The contents of the flask were then filtered through a medium-fritted glass filter into a 31 three-necked flask while maintaining a dry inert atmosphere. The flask containing the filtrate was fitted with distillation apparatus and tris(N-methylamino)methylsilane was collected at $149-151°C$. The product was a clear liquid at room temperature.

The infrared (IR) spectrum showed absorption for N—H (3400 cm^{-1}), N—CH$_3$ ($950-1150$ cm^{-1}), C—H (2900 cm^{-1}), and SiCH$_3$ ($750-950$ cm^{-1} and 1250 cm^{-1}). Nuclear magnetic resonance (NMR) (CDCl$_3$) showed peaks at 2.65 ppm (N—CH$_3$) and 0.12 ppm (Si—CH$_3$).

ANAL. Calcd for C$_4$H$_{15}$NSi: C, 36.1%; H, 11.3%; N, 31.5%; Si, 21.0%. Found: C, 32.9%; H, 11.8%; N, 31.6%; Si, 21.5%.

Synthesis of Polycarbosilazane Resin

In the polymerization step, quantities of tris(N-methylamino)methylsilane (15 mL) were placed in the apparatus shown in Figure 1, which is basically a total reflux distillation system. The temperature was raised and the monomer polymerized upon passing over glass raschig rings at a temperature of $520°C$ for a period of either 1.5, 3.0, or 4.5 h.

After completion of the polymerization step, the resin was separated from lower boiling impurities by distillation at $450°C$ and atmospheric pressure followed by distillation at $300°C$ under vacuum supplied by a water aspirator. The distillations were carried out by modification of the apparatus shown in Figure 1. The condenser was removed and the polymer sample placed in the heating tube which was then equipped with distillation apparatus.

The polycarbosilazane resin produced by this technique was a yellow to reddish-brown, brittle, transparent product that was soluble in conventional organic solvents such as methylene chloride and chloroform.

The infrared (IR) spectrum showed absorption for NH (3500, 1630, and 1170 cm^{-1}), N—CH$_3$ (1050 cm^{-1}), CH (3000 cm^{-1}) and Si—CH$_3$ (1250 and $850-890$ cm^{-1}). Nuclear magnetic resonance (NMR) (CDCl$_3$) showed peaks at 1.40 ppm (SiCH$_3$) and 3.10 ppm (N—CH$_3$).
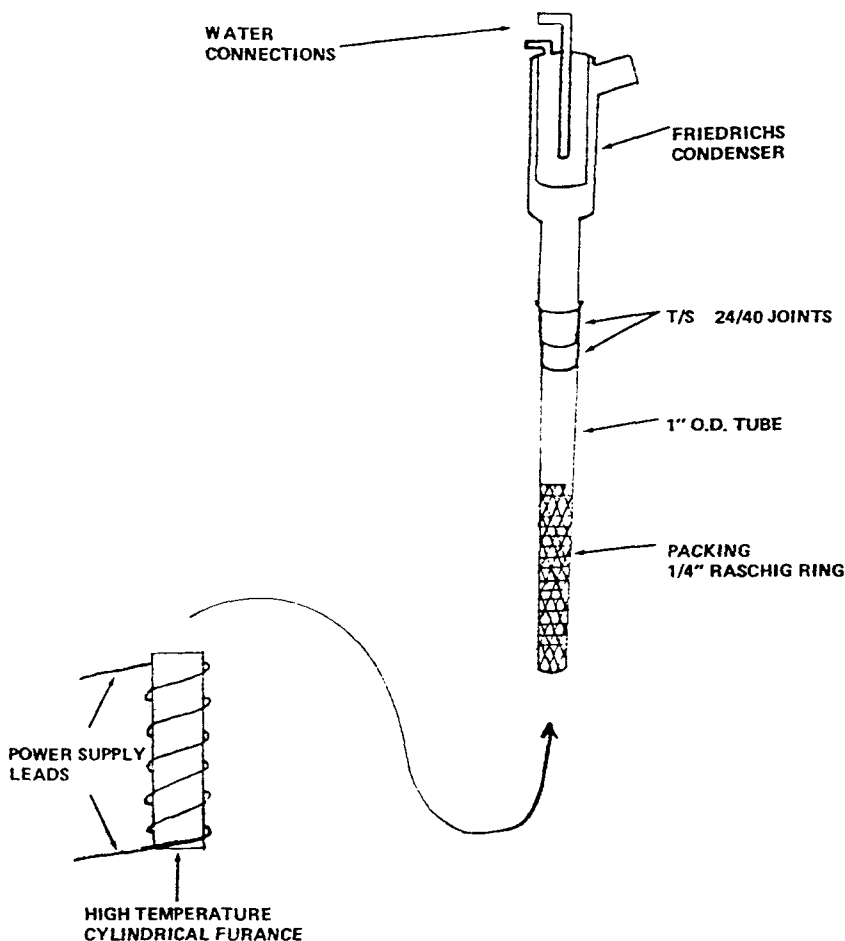
Fig. 1. High temperature polymerization system.

Preparation of Pyrolyzed Fibers

Precursor fibers for $Si_x N_y C_z$ fiber preparations were hand drawn from the polycarbosilazane resin melt maintained in an inert atmosphere at 220–250°C by touching the surface of the melt with a glass rod and stretching to obtain fibrous material.   Lengths up to 6 ft were obtained with diameters of 0.5–4 mils by controlling the drawing rate.

Immediately after drawing, precursor fibers of the desired geometry (diameter of 0.5–4.0 mils and length of about 4 in.) were placed in an environmental chamber and humidity conditioned at 100°C and 95% relative humidity for 20 h.   Some of the conditioned fibers were placed under tension in ceramic holders and heated in a furnace under nitrogen from room temperature to 1200°C in 7 h followed by heating from 1200°C to 1500°C during 2 h.   A weight loss of 38% occurred during pyrolysis of the precursor fibers to shiny-black $Si_x N_y C_z$ fibers.

Physical and Chemical Properties Determination

Infrared (IR) spectra of the polycarbosilazane resin were determined using a Perkin-Elmer 137 Sodium Chloride Spectrophotometer with the sample in solution and placed between sodium chloride plates. IR spectra of tris(N-methylamino)methylsilane were determined by placing the liquid monomer between sodium chloride plates.

Nuclear magnetic resonance (NMR) spectra of the monomer and resin were prepared using a Varian EM 300 system with deuterated chloroform as the solvent and tetramethylsilane as an external reference.

Gel permeation chromatography (GPC) was used to determine weight average molecular weights ($\overline{M}_w$). A Water Model 244 GPC with an R 401 Differential Refractometer was used with THF as the solvent. The GPC runs were carried out at room temperature using four columns (two of 500 A and two of 1000 A). The flow rate was 1 mL/min. The molecular weights were determined using the universal calibration curve as described elsewhere.[7] Intrinsic viscosities for use in calculating the $\overline{M}_w$ were determined using an Ulbelohde viscometer. The solvent was THF and the temperature was 30°C.

Chemical analyses of the monomer and precursor resin were made for C and H by a combustion technique developed by the authors. This technique will be presented in a future paper. A combustion–volumetric method was used to determine the silicon content, and the Kjeldahl technique was used to determine the nitrogen content.

Elemental analyses of silicon carbide–silicon nitride fibers for C, H, and O were determined by sodium carbonate fusion and Si by a combustion–gravimetric method.
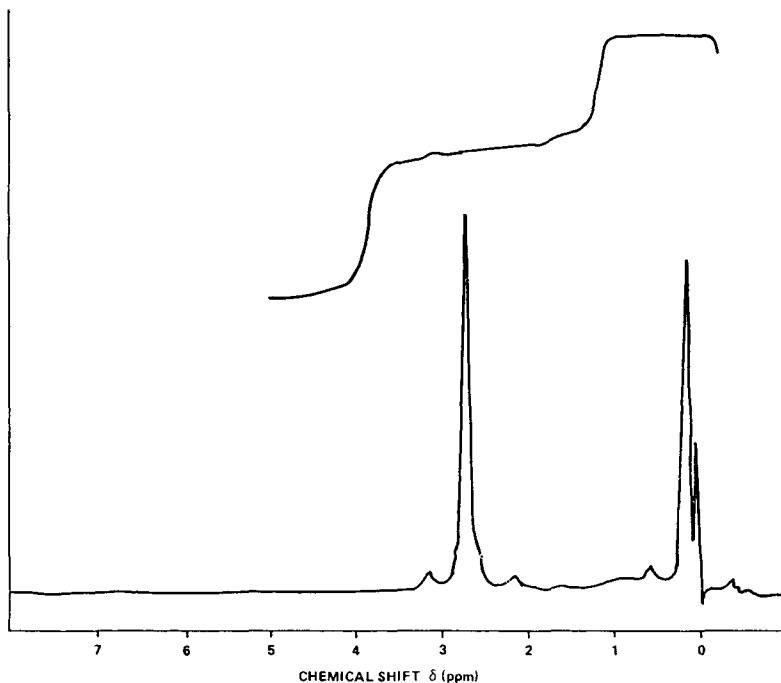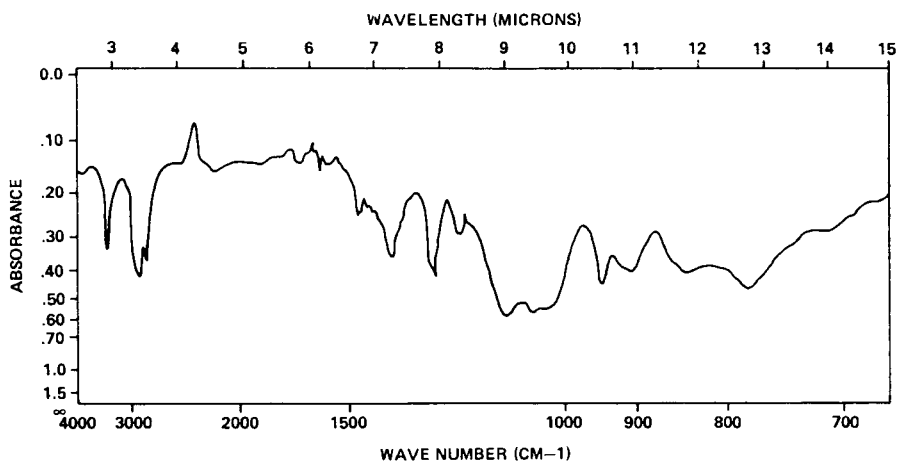

Fig. 2. NMR spectrum of tris(N-methylamino)methylsilane.

WAVELENGTH (MICRONS)

Fig. 3. Infrared spectrum of tris(N-methylamino)methylsilane.

Softening points of the polycarbosilazane precursor were determined using a Fisher-John melting point apparatus.

A H-15 Mettler Balance was used to determine the weight loss on conversion of precursor polymer to $Si_x N_y C_z$ fibers. Diameters of both the conditioned precursor fibers and the pyrolyzed fibers were measured using a Leitz Wetzlar microscope and a Bausch and Lomb stage micrometer.

Mechanical properties of the prepyrolyzed and pyrolyzed fiber specimens were calculated from fiber data taken using an Instron 1100 series system with an installed 10–30-g-range load cell.

Electrical resistivities of the pyrolyzed fibers were measured by using a Hewlett-Packard 4329A High Resistance Meter. Structural analyses were made using a Phillips X-ray diffractometer with copper radiation source operated at 40 kV, 40 mA, 20/min scan and 250 counts/min.

RESULTS AND DISCUSSION

Monomer Synthesis and Characterization

Monomeric tris(N-methylamino)methylsilane was synthesized by the reaction of methylamine with methyltrichlorosilane as shown below:

$$CH_3SiCl_3 + 6 CH_3NH_2 \rightarrow CH_3Si (NHCH_3)_3 + 3[CH_3N^+H_3]Cl^- \qquad (1)$$

In the procedure described in this paper, liquid methylamine was condensed into a reaction flask containing petroleum ether which was cooled to −30°C. This was followed by the dropwise addition of methyltrichlorosilane. Verbeek syn-

TABLE I
Elemental Analysis of Tris(N-methylamino)methylsilane

Element	Theoretical wt %	Experimental wt %
N	31.5	31.6
H	11.3	11.8
Si	21.0	21.5
C	36.1	32.9

thesized the monomer by reacting gaseous methylamine with methyltrichlorosilane dissolved in petroleum ether at 40°C.[3] The procedure used by Tansjo was to add methyltrichlorosilane to an ice-cooled solution of methylamine dissolved in ether.[5]

The success of the reaction was confirmed by NMR (Fig. 2) and IR spectroscopy (Fig. 3). Infrared spectral assignments were made for the following groups: N—H (3400 cm^{-1}), N—CH$_3$ (950–1150 cm^{-1}), C—H (2900 cm^{-1}), and Si—CH$_3$ (750–950 cm^{-1}, 1250 cm^{-1}). NMR spectra showed peaks at 0.12 ppm (SiCH$_3$) and 2.65 ppm (N—CH$_3$).

Further evidence for the success of the reaction was provided by elemental analysis (Table I). The weight percent of C, H, N, and Si was found to be 32.9%, 11.8%, 31.6%, and 21.5%, respectively. Theoretical values were 36.1% (C), 11.3% (H), 31.5% (N), and 21% (Si).

Polycarbosilazane Synthesis and Properties

The polymerization of tris(N-methylamino)methylsilane was carried out at 520°C for 1.5, 3.0 and 4.5 h in order to determine the effect of reaction time on the molecular weight. GPC was used to determine the weight average molecular weight. A typical molecular weight distribution curve is shown graphically in Figure 4. The previously described reaction times resulted in molecular weights of 1533, 2472, and 4222, respectively (see Fig. 5 and Table II).

The polymer was characterized by NMR (Fig. 6), IR (Fig. 7), elemental analysis, and softening point determination. Infrared spectral assignments[9,-11] were made for the following functional groups: NH (3500, 1630 and 1170 cm^{-1}), N—CH$_3$ (1050 cm^{-1}), C—H (3000 cm^{-1}), and Si—CH$_3$ (1250 and 850–890 cm^{-1}). Nuclear magnetic resonance spectra were obtained using tetramethylsilane as an external reference. Peaks exist at 1.40 ppm (Si—CH$_3$) and 3.10 (N—CH$_3$). Elemental analysis (Table III) showed the presence of C, Si, N, and H. Weight
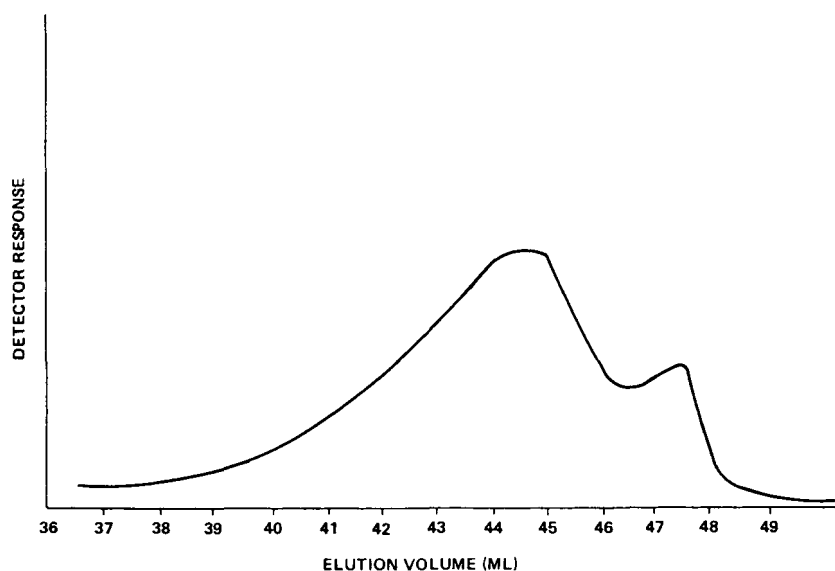

Fig. 4. Gel-permeation chromatography of polycarbosilazone resin.
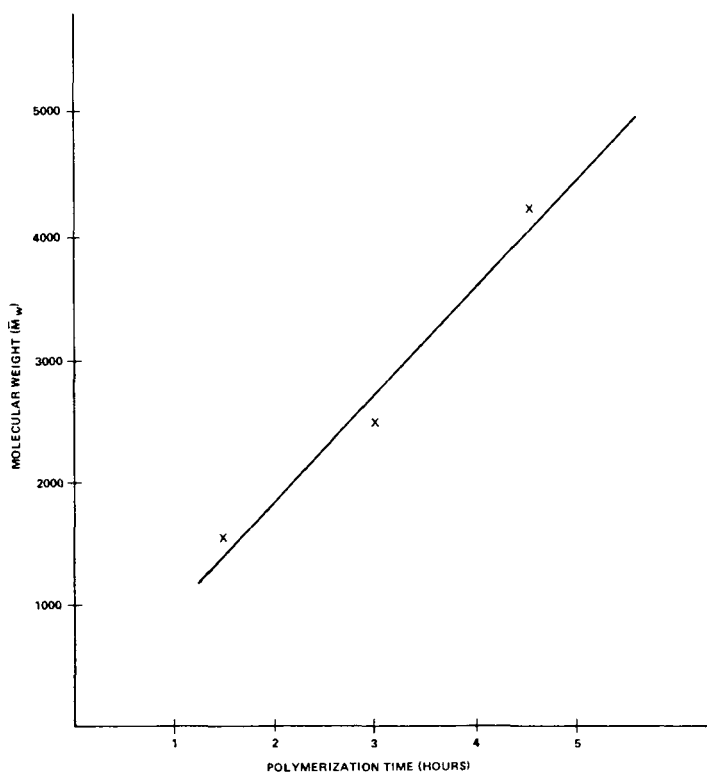
Fig. 5. Polycarbosilazone resin weight average molecular weight versus polymerization time.

TABLE III
Polycarbosilazane Resin Elemental Analysis

Element	Theoretical wt %	Experimental wt %
N	25.4	21.9
H	9.1	9.7
Si	30.5	29.6
C	34.9	35.4

percents of 34.9, 30.5, 25.4, and 9.1 were obtained, respectively. The softening point of the polycarbosilazane precursor was determined to be 140°C. This compares favorably with data reported by Verbeek.[3]

The tensile strength of the precursor fiber versus fiber diameter is given in Table IV. Diameters of 0.52, 1.74, and 4.97 mils resulted in tensile strengths of 13,000, 4,000, and 1,800 psi, respectively. These data show that the amount

TABLE II
Effect of Polymerization Time on Molecular Weight

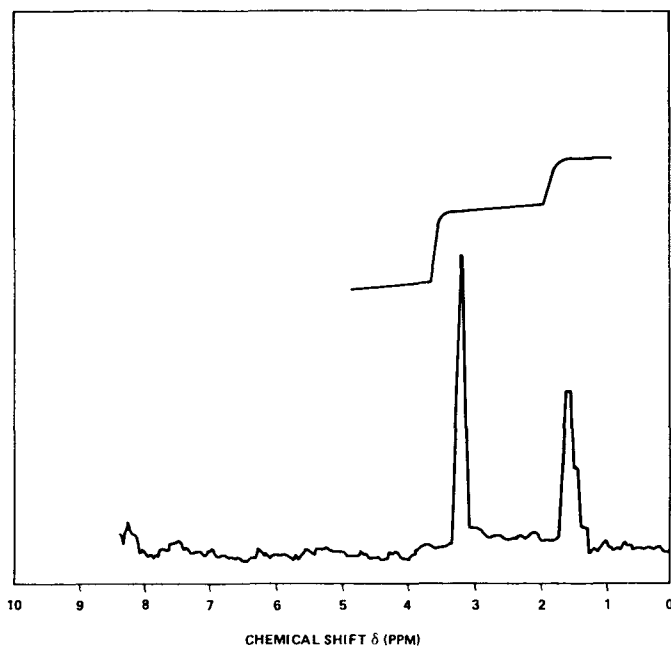| Polymerization time (h)	Weight-average molecular weight $\overline{M}_w$
1.5	1533
3.0	2472
4.5	4222

Fig. 6. NMR spectrum of polycarbosilazone (solvent C_6D_6, at 30 MHz).

of tension that may be applied to the precursor fiber to orient the molecular chains during pyrolysis to increase the tensile strength of the $Si_xN_yC_z$ fiber is limited by the fiber diameter.
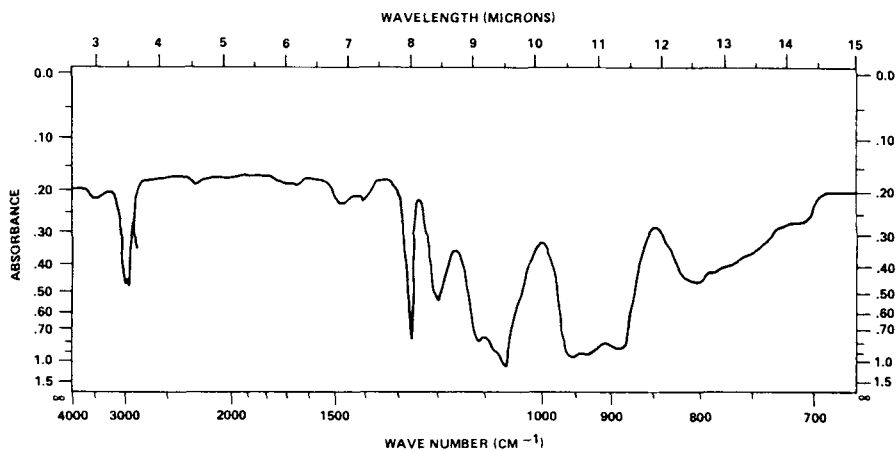

Fig. 7. Infrared spectrum of polycarbosilazone resin.

TABLE IV
Prepyrolyzed Fiber Tensile Strengths and Diameter

Fiber diameter (mil)	Tensile strength (psi)
0.52	13,800
1.74	4,000
4.97	1,800

TABLE V
Pyrolyzed Fiber Resistivity Data

Fiber	Cross-sectional area (cm^2)	Length (cm)	Resistance (Ω)	Resistivity ($\Omega \cdot$ cm)
1	2.16×10^{-6}	1.59	5.0×10^{14}	$7.2 \times 10^{+8}$
2	2.16×10^{-6}	1.27	3.9×10^{14}	$6.6 \times 10^{+8}$

Silicon Carbide–Silicon Nitride Fiber Preparation and Properties

$Si_x N_y C_z$ fibers were prepared by the pyrolysis of humidity conditioned precursor fibers at temperatures ranging from ambient to 1200°C. The percentage weight loss during pyrolysis was determined to be 38%, which is within the weight loss range of other precursor materials on conversion to inorganic product.[3,12]

The silicon carbide–silicon nitride material was subjected to X-ray and elemental analyses. The pyrolyzed material was found to be amorphous and to consist of Si, C, N, and O. It is most likely a homogeneous mixture of silicon carbide–silicon nitride and/or carbon, as was reported by Verbeek.[3]

The electrical resistivites of silicon carbide–silicon nitride fibers are recorded in Table V and were calculated from the equation given below[13,14]:

$$\rho = RA/L \tag{2}$$

where ρ = electrical resistivity, R = total resistance of conductor, A = cross-sectional area of conductor in direction perpendicular to direction of current flow, L = length of conduction path.

The average resistivity value obtained for $Si_x N_y C_z$ fibers (7×10^8 Ω·cm) lies within the range of semiconductors (10^{-3}–10^{10} Ω·cm) but approaches the value of true insulators which is $\geq 10^{12}$ Ω·cm.[15]

The relationship of tensile rupture modulus (E_I) to fiber diameter (d) for
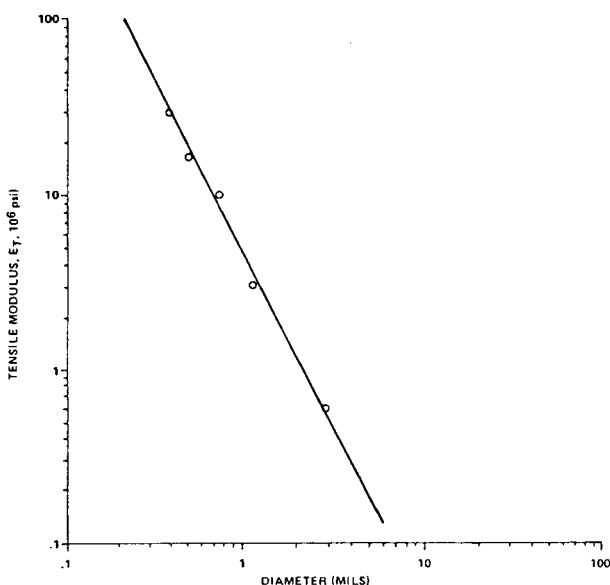

Fig. 8. Tensile rupture modulus of pyrolyzed fibers versus diameter.

TABLE VI
Physical Properties of Pyrolyzed $Si_xN_yC_z$ Fibers vs. Fiber Diameter

Diameter d (mil)	Tensile strength (10^3 psi)	Elongation (%)	Tensile Rupture Modulus E_T, (10^3 psi)
0.39	105.0	0.36	29.2
0.50	70.7	0.44	16.1
0.88	38.0	0.64	5.9
1.15	31.5	1.04	3.0
2.90	1.18	0.20	0.59

silicon carbide–silicon nitride fibers obtained by the pyrolysis of the precursor material is illustrated in Figure 8 and summarized in Table VI. Using the five data points shown in Table VI, a log–log plot of E_T (10^6 psi) vs. fiber diameter was used to derive the following mathematical relationship:

$$E_T = 4.5d^{-2} \qquad (3)$$

The tensile rupture modulus was found to decrease as the fiber diameter increased. This phenomenon has also been observed for silicon carbide fibers.[16] An increase in surface defects as the diameter increases[17] is most likely the cause for this occurrence. The development of small diameter fibers has been emphasized, because greater fineness allows wider distribution of the fibers in the matrix.[17] $Si_xN_yC_z$ fibers are predicted to provide a high modulus at small diameters as indicated by application of eq. (3) or extrapolation of data in Figure 8. For example, a fiber diameter of 5.5 μm extrapolates to a modulus of 100×10^6 psi.

Tensile strength and elongation versus the fiber diameter data are presented in Table VI. The tensile strength, which ranges from 1.18×10^3 psi (2.9-mil diameter) to 105×10^3 psi (0.39-mil diameter), was found to increase as the fiber diameter decreases. This trend has been noted for carbon[18] and silicon carbide[16] and is most likely due to an increase in surface defects as the diameter increases.[17] Data in Table VI shows that the silicon carbide–silicon nitride fibers have a low percent elongation (0.2–1.04%).

CONCLUSION

A technique for preparing silicon carbide–silicon nitride based on a technique developed by Verbeek[3] is described. The resin weight average molecular weight was found to be a function of time and reached a value of 4222 after polymerizing tris(N-methylamino)methylsilane at 520°C for 3 h.

The $Si_xN_yC_z$ fibers are comparable to other high strength fibers in terms of mechanical properties. For example, its tensile modulus (29×10^6 psi) is comparable to that of other reinforcement fibers such as alumina, boron nitride, silicon carbide, and graphite, which have tensile moduli of 25, 12, 65, and 55×10^6 psi, respectively. However, the electrical resistivity value of silicon carbide–silicon nitride is about 10^{12} greater than that obtained for graphite.

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