

Polymer-Derived SiBN Fiber for High-Temperature Structural/Functional Applications

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We report the fabrication of a SiBN fiber through pyrolysis of a novel polyborosilazane polymer. Preliminary findings show that this new ceramic fiber demonstrates structural/functional properties with high mechanical strength, a low and thermally stable dielectric constant, and excellent high-temperature resistance. Because of this combination of desirable properties, SiBN ceramic fiber has the potential to resolve a wide number of today's material challenges in high-temperature, radar-wave-transmitting applications.

The rapid development of the aerospace industry and the generation of new high mach number aircrafts require new materials for electromagnetic windows or radomes to meet the stringent requirements of greater speed, higher temperature, and longer flight times. Such materials must have low density, high thermal stability, and a low and thermally stable dielectric constant with high mechanical strength. The ceramic fiber reinforced nitride ceramic matrix composites (FRCMCs) offer several advantages, such as high working temperatures, low ablation, and high mechanical strengths in high-temperature applications.^[1,2] However, the mechanical and physical performances of FRCMCs are greatly influenced by the properties of the reinforcing fibers. The thermomechanical and -chemical properties of fibers always prescribe the atmosphere, temperature, and weaving capabilities in composite manufacture.^[1] Therefore, performances of FRCMCs depend on the right selection of fibers with proper chemical and physical properties.^[1,3] For composites to be useful in the above-described environments, the fibers should be lightweight, structurally stable, and mechanically strong at elevated temperatures. Moreover, they must possess excellent and thermally stable dielectric properties.

Clearly, the selection of fibers suited for such applications is limited. Those fibers prepared from polymer pyrolysis are particularly attractive because of their fine diameter and flexibility to allow weaving and braiding. Furthermore, with this method, fiber properties, including density, dielectric properties, and tensile strength, can be tailored through control of the starting polymer and the curing and the pyrolysis steps.^[3,4]

Presently, SiC fibers, quartz fibers, Si₃N₄ fibers,^[5,6] and BN fibers^[7–10] are the fibers available with potential applications in such areas. Each of these fibers has its individual peculiarities in properties. SiC fibers are the well-established fibers with excellent mechanical performances and thermal resistance, however, the inefficient dielectric properties resulting from the high carbon content cannot meet the practical requirements.^[11,12] Quartz fibers are one of the most commonly used reinforcements in radome composites because of their excellent dielectric properties.^[13–16] However, their low mechanical property at high temperature is the critical drawback, limiting their application to more hostile conditions.^[11,16,17] In addition, quartz fibers are intrinsically prone to crystallization at high temperatures, leading to the low preparation temperature of the composites. This results in the low bonding strength between the fiber and the ceramic matrix, and thus the high mechanical performance of the composites cannot be fully used. BN fibers exhibit low density, excellent high-temperature resistance, low and thermally stable dielectric constants; however, their low mechanical strengths and ineffective oxidation resistance at high temperatures make them unsuitable, at least presently, for use as reinforcement in FRCMCs. Generally, Si₃N₄ fibers have higher mechanical strengths than BN fibers; however, the thermal resistance of Si₃N₄ fibers is inferior to BN fibers and the dielectric properties should be improved for practical use.^[18] Therefore, it is important to keep the dielectric, mechanical properties, and thermal stability balance to meet high-temperature, radar-wave-transparent applications.

SiBN fibers, combining the merits of Si₃N₄ fibers and BN fibers, are expected to possess comprehensive performances

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with high mechanical properties, good dielectric behaviors, and excellent thermal resistance, and therefore, may be qualified as the candidate for reinforcement in high-temperature, radar-wave-transparent ceramic composites. To the best of our knowledge, there is no previous reports on the preparation and properties of SiBN fibers.

As is known, fabrication of ceramic fiber from polymer pyrolysis typically involves the following steps: polymer synthesis, fiber forming and curing, followed by pyrolysis of the cured fibers.^[19] Among them, the synthesis of an appropriate processable precursor is an essential prerequisite. It is required that the polymer is composed of the target elements in a desired chemical environment in the final ceramics. At first thought, the precursor for the SiBN fiber should be carbon free; however, the polyborosilazane polymer without any organic groups is extremely reactive. The guarantee of controllable synthesis and spinning processes of such a precursor can be very difficult. With this in mind, we used methyl-containing polyborosilazane as the preceramic precursor for the SiBN ceramic fiber. The decarburization was carried out in the subsequent steps. For example, curing the green fibers with Cl-containing species would preliminarily reduce the carbon content through loss of the organic groups. Then, carbon would be further decreased by pyrolyzing the cured fibers in ammonia atmospheres.^[20,21]

The processable preceramic polyborosilazane was synthesized in a one-pot process by mixing boron trichloride (BTC), dichloromethylsilane (DCMS), and hexamethyldisilazane (HMDZ) in a given molar ratio. The reaction mainly involves the condensation of Si-Cl and B-Cl with N-SiMe₃ followed by SiMe₃Cl evaporation.^[22-25] After in situ distillation of the solvent, by-products, and low-molecular-weight oligomers, the moisture- and air-sensitive product was collected as a colorless transparent solid. This route has an advantage over other methods, since it starts from easily available molecular educts that were directly condensed to the preceramic polymers, without the steps of oligomeric intermediates and separate processes of by-product elimination. The as-obtained polyborosilazanes have typical melting points of 85–98 °C and show good melt spinnability. Green fibers with diameters of approximately 15 μm and a continuous length >1000 m can easily be obtained at 128–140 °C under inert atmospheres. The as-spun fibers were then exposed to BTC vapor to make them infusible. The sufficiently cured fibers were pyrolyzed up to 1000 °C in a stream of dry NH₃ and additionally heated to 1500 °C in a nitrogen atmosphere to produce white SiBN fibers in a yield of 52 wt %.

The compositions of the green, cured, and final ceramic fiber were measured and are listed in Table 1. The high carbon content of 21.73 wt % in the green fibers originates from the large amount of monomer CH₃. It reduced to 13.98 wt % after the fiber was cured, which is beneficial to carbon removal in the pyrolysis step. The

carbon decrease during the curing process results from the readily reaction between polymer -SiMe₃ and B-Cl in the curing agent, with the formation of volatile SiMe₃Cl. Since all of the carbon in the precursor exists as pendant or end group Si-CH₃, as confirmed by the FTIR spectrum (see below), they can easily be eliminated through pyrolysis in an NH₃ atmosphere, with only 0.1 wt % in the final SiBN fibers. The smooth carbon removal is ascribed to the reaction between Si-Me and ammonia N-H to release CH₄ gas. The fibrous shape also provides an advantage in carbon removal, since pyrolysis of bulk polyborosilazane under the same conditions led to SiBN ceramics with 0.5 wt % carbon, as in our previous reports.^[26,27] Besides the expected Si, B, and N, the low-content O was found to be contaminated during the transfer of the samples. If the O and C contents are neglected, the obtained SiBN fiber has an apparent composition of Si_{1.41}BN_{2.86} or (BN)(Si₃N₄)_{0.47}, with no excessive elemental Si. The molar ratio of B/Si=1:1.4 of the cured fiber remains constant during the polymer-to-ceramic transformation, implying the polymer backbone survives the ceramization process.

Figure 1 shows FTIR spectra of the as-spun polymer fiber and the as-pyrolyzed SiBN ceramic fiber. The main absorption peaks of the green fiber can be assigned as follows: 3427/1179: N-H, 2955/2858: C-H, 2126: Si-H, 1386: B-N, 913: Si-N, and 1252 cm⁻¹: Si-C. The polyborosilazane possesses a Si-N-B bridge with some borazinic rings, as implied by FTIR spectroscopy and other characterization methods, including ¹¹B and ²⁹Si NMR spectroscopy. It was reported that the thermally stable rigid borazine may act as an inhibitor, suppressing structural changes in the SiBNC ceramics.^[28] The borazinic structural units in the polyborosilazane are undoubtedly favorable to the thermal and mechanical stabil-

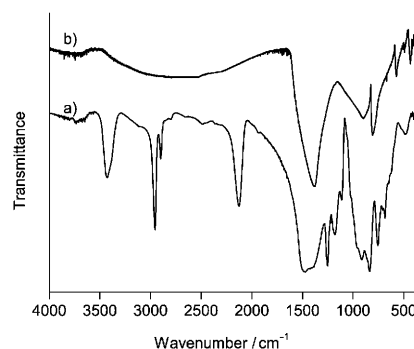


Figure 1. IR spectra of the as-spun polyborosilazane fiber (a) and the as-pyrolyzed SiBN fiber (b).

Table 1. Elemental analysis of the green, cured, and SiBN fibers.

Material	Composition [wt %]							Si/B ^[a]	N/B ^[a]	Total
	Si	B	N	C	H	O	Cl			
green fiber	32.42	5.19	31.84	21.73	8.89	0.36	0	2.40	4.73	100.43
cured fiber	25.97	7.11	23.37	13.98	5.38	ND ^[b]	23.75	1.41	2.53	99.56
SiBN fiber	42.73	11.76	43.62	0.1	0	0.48	0	1.40	2.86	98.69

[a] Atomic ratios. [b] ND: not determined.

ity of SiBN fibers. The absorption peaks of the organic groups in the precursor fibers disappeared after they were pyrolyzed, indicating the full inorganic conversion of the cured fibers. The main IR absorptions peaks in the SiBN fibers are 901 and 1380/801 cm^{-1} , which are characteristic of Si–N and B–N, respectively.

To have practical potential, especially for application in high-temperature, radar-wave-transparent composites, the new ceramic fiber must have long-term thermal stability and corrosion resistance. Preliminary results indicated that the SiBN fibers can easily withstand temperatures up to 1700 °C in 0.1 MPa N_2 and up to 1400 °C in flowing air for 2 h, while retaining most of the mechanical and dielectric properties.

XRD patterns of the thermally aged SiBN fibers show that the fibers remain amorphous up to 1700 °C in nitrogen atmospheres. This is consistent with the results reported for the ceramics in the system SiBNC.^[29–33] Compared with the crystallization temperature of about 1200 °C of the binary Si_3N_4 ceramics,^[34] the retarded crystallization of SiBN fiber can be ascribed to the incorporation of boron. According to Müller,^[31] SiBNC ceramics with 5–17 wt% boron are protected from thermal degradation at elevated temperatures. The SiBN fiber in the present work has a boron content falling in this range and thus excellent thermal resistance can be expected.

Stability to oxidation is the primary concern when regarding corrosion resistance at high temperatures.^[11] Oxidation resistance of the SiBN fibers was examined by annealing them at 1400 °C for 2 h in flowing air. The fibers were fairly resistant to oxidation. It is interesting that the carbon-free SiBN fibers present similar oxidation behavior to the carbon-containing SiBN_3C fibers.^[11] The formation of protective two-layer oxidation product with compositional difference was also observed by scanning electronic microscopy (SEM) in the oxidized SiBN fibers. The oxide layer was dense and intact with no evidence of porosity or fracture. Obviously, the similar oxidation behavior of the two fibers does not imply the role of carbon can be underestimated, since they were not oxidized under the same conditions.

As the SiBN fiber does not tend to crystallize up to 1700 °C in nitrogen environments and up to 1400 °C in oxidizing atmospheres, it is expected that the room-temperature tensile strength is mostly retained under such conditions. Table 2 lists the mechanical properties of the as-prepared SiBN fibers and those treated at different elevated temperatures. At room temperature, the fibers show average tensile strength of 1.83 GPa and elastic modulus of 196 GPa. Whereas the N_2 -annealed fibers show almost as high tensile strength as the as-pyrolyzed ones, the oxidized fiber has a

relatively lower strength. The most possible mechanism is related to the combined effect of tensile residual stresses formed during oxidation and the oxide flake encouraging the crack growth.^[35] Although these values are suitable for use as fibrous reinforcement in FRCMCs, they are much lower than those of the SiBN_3C fibers reported by Jansen et al.^[11] This may be ascribed to the positive role of carbon incorporated in enhancing the mechanical properties of the SiBN_3C fibers.^[36–39]

The mechanical property of the ceramic fibers can also be mirrored by their micromorphology, as shown in Figure 2. As can be seen, the fibers are dense without any detectable flaw. The fiber density, determined by pycnometry, is 2.2 gcm^{-3} . Being amorphous, the fibers exhibited a smooth surface with a glassy section, which is an important element for reinforcement by pullout in ceramic fiber composites.^[30,40] This implies that the SiBN fiber is suitable for use as reinforcement in FRCMCs, especially for those used at high temperatures.

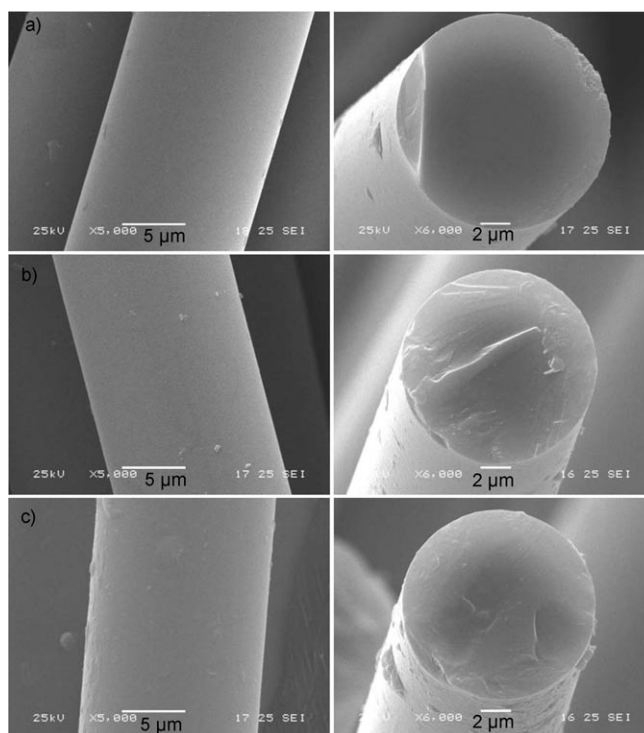


Figure 2. SEM images of the as-pyrolyzed (a) and SiBN fibers annealed at 1700 °C in N_2 (b) and at 1400 °C in air (c).

Table 2. Mechanical properties of the as-prepared and annealed SiBN fibers.

Material	Tensile strength [GPa]	Elastic modulus [GPa]	Diameter [μm]	Failure strain [%]
fiber as-pyrolyzed	1.83	196	11.8	0.93
fiber annealed at 1700 °C/ N_2	1.80	203	11.6	0.89
fiber annealed at 1400 °C/air	1.65	189	11.8	0.86

Apart from the good thermal and mechanical behavior, SiBN fibers also exhibit superior dielectric properties (Table 3). To the best of our knowledge, no standard methods are currently available to directly evaluate the dielectric properties of fiber

Table 3. Dielectric properties ($f=10$ GHz) of SiBN fiber and quartz fiber at different temperatures.

	Room temperature		1200 °C	
	SiBN fiber	Quartz fiber	SiBN fiber	Quartz fiber
dielectric constant	4.36	3.12	5.12	3.02
loss tangent	0.0042	0.0036	0.0086	0.034

materials. Hence, we used a powdered sample of SiBN fiber for dielectric measurements. The feasibility of this method was validated by the measurement of the known dielectric parameters of quartz fiber under the same conditions. The dielectric properties of the two types of fibers were measured at room temperature and at 1200 °C, the maximum operating temperature of the measuring instrument used. Regarding the dielectric constant and loss tangent, both fibers demonstrated comparable values at ambient temperature. However, the amorphous SiBN fibers have lower changes in dielectric constants, especially in loss tangent value, than the quartz fibers with temperature rise. This is very important for high-temperature, radar-wave-transparent materials. The superior dielectric properties of SiBN fiber may result from the compositional Si_3N_4 and BN phases, which are typical dielectric materials themselves. As is known, carbon, in particular, free carbon, is very detrimental to the dielectric performances, especially to the loss tangent value.^[41] Undoubtedly, the extremely low carbon content, as discussed above, favors decreasing the dielectric values of SiBN fibers. In addition, excessive elemental Si is also disadvantageous to the dielectric properties, owing to its semiconducting behavior. In the SiBN fiber with near stoichiometric composition $(\text{BN})(\text{Si}_3\text{N}_4)_{0.47}$, there almost exists no free silicon. This acts as another important factor leading to the excellent dielectric properties of this ceramic fiber.

In summary, a novel, high performance SiBN fiber was prepared by polymer pyrolysis using carbon-containing polyborosilazane as the precursor. The obtained SiBN fiber exhibits extraordinary thermal resistance. Significant mechanical strength loss was not observed after treating the fibers at 1700 °C in nitrogen or at 1400 °C in air. The near stoichiometric composition with low carbon content delivers the fiber excellent and thermally stable dielectric properties. This desirable combination of properties suggests that SiBN fiber holds great promise for reinforcement application in high-temperature, radar-wave-transparent composites.

Experimental Section

Polymer synthesis: All reactions were carried out in a dry nitrogen atmosphere by using standard Schlenk techniques. All of the monomers were handled without air contact and stored in a moisture-free environment. BTC, DCMS, and HMDZ were purchased from Guangming Special Gas Corp., Xinghuo Chemical Corp., and Guibao Chemical Corp., respectively. BTC was maintained in *n*-hexane in the refrigerator prior to use. Hexane was dried with sodium–benzophenone mixture under reflux. DCMS and HMDZ were distilled before use. Typically, the molar ratio

between monomers was set at 1:2.2:7 (BTC/DCMS/HMDZ). BTC in 1 M hexane was introduced with a syringe from the bottle and injected into a pre-cooled reactor through a septum. DCMS was added to the reactor in the same manner. HMDZ was injected into a dropping funnel with a septum and carefully added dropwise to the mixed solution under vigorous stirring, whereby a cloudy solution without precipitation was observed. The temperature of the mixture was kept below -10 °C during the addition of monomers. After the addition of HMDZ, the reaction mixture was heated to 200–350 °C and held at the maximum temperature for 6–20 h. The final traces of starting reagents, solvent, by-products, and low-molecular-weight oligomers were removed at 100–200 °C by application of a vacuum for 1 h. Simply cooled to ambient temperature, the product was collected as a colorless transparent bulky solid that is sensitive to moisture and air. The yield of product was typically >92% of theory, based on the weight of BTC and DCMS. The bulk product was transferred into a glove box, placed in a vial full of nitrogen, and finally stored in vacuum dry-sealing desiccators.

Polymer fiber preparation: The polymer green fibers were prepared with a lab-scale melt-spinning apparatus set up in a glove box filled with 99.999% ultra-high pure nitrogen. The as-synthesized polymer was fed into an extruder, where it was heated, sheared, and pressured through a filtering system to eliminate any gels or unmelts that might be present in the extrudate. The molten polymer then passed through a spinneret that had a single 0.20 mm capillary. The extrudate flow was then uniaxially drawn in a nitrogen atmosphere into a filament, which was subsequently stretched and collected on a rotating spool.

Fiber curing and pyrolysis: The curing and pyrolysis of the polymer fibers were performed in the same high-temperature alumina tube furnace. Before adding to the polymer fibers, the furnace tube was purged by a vacuum and subsequently filled with ultra-high pure nitrogen repeatedly at room temperature to remove the residual air. The polymer fibers were cured by passage of a vapor of BTC with dry nitrogen for several minutes in the tube furnace. The tube furnace was then heated by a program controller to 1000 °C under flowing 99.999% ultra-high pure ammonia, with a heating rate of 200 °C h^{-1} , and then to 1500 °C in a flowing purified nitrogen atmosphere at 250 °C h^{-1} . After held at the final temperature for 2 h, the furnace was simply cooled in ambient air to room temperature to provide white SiBN ceramic fibers.

Characterization: Silicon was analyzed by inductively coupled plasma-atomic emission spectrum in an Arl 3580B spectrometer after digesting the ceramic samples with a mixture of bases. Boron and chlorine were measured by a chemical titration method. Quantitative analysis of nitrogen, oxygen, and hydrogen was carried out in a Leco TCH-600 N/H/O determinator. Carbon content was measured by using a Leco CS-600 C/S analyzer. FTIR spectra were obtained with a Nicolet Avatar 360 instrument as a KBr pellet. NMR spectra of the polymer were recorded in CDCl_3 by using a Bruker Advance 400 MHz instrument. SEM images of the fiber morphology were obtained by using a JEOL JSM-5600 LV electron microscope. The phase structure of the obtained pyrolyzed specimens was characterized by D8 ADVANCEX powder X-ray diffraction, using $\text{CuK}\alpha$ radiation. Single filament tensile properties were determined at room temperature with a gauge length of 25 mm using an YG-type tensile strength tester made by Jiangsu Taicang Textile Instruments, China. Forty single filaments taken from bundles were tested. Failure strain, elastic modulus, and tensile strengths were measured from data of breaking load-elongation curve records and cross-sectional area calculations. The average failure strain and elastic modulus were calculated from the 40 as-obtained values. The statistical variability of the strength was reported in terms of Weibull statistics.^[42] An average tensile strengths of the SiBN fibers was then estimated for a failure probability $P=0.589$. The dielectric properties of the powder of SiBN fibers and quartz fibers at 10 GHz were determined at room temperature and at 1200 °C by HPD -type high-temperature dielectric parameter measurer using a cavity resonator method, respectively. Before the dielectric measurements, fibers were ground into a powder and pressure molded into a cylinder sheet with a size of (49.8 ± 0.1) mm in diameter by 1–16 mm in height. The average data were calculated from five tests.

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