Mechanical and Dielectric Properties of Two Types of Si$_3$N$_4$ Fibers Annealed at Elevated Temperatures

Jie Zhou, Fang Ye, Xuefeng Cui, Laifei Cheng *, Jianping Li, Yongsheng Liu and Litong Zhang

Science and Technology on Thermostructural Composite Materials Laboratory, Northwestern Polytechnical University, Xi'an 710072, China; 13628013651@163.com (J.Z.); yefang511@nwpu.edu.cn (F.Y.); cuixuefeng@nwpu.edu.cn (X.C.); ijianping@163.com (J.L.); yongshengliu@nwpu.edu.cn (Y.L.); zhanglt@nwpu.edu.cn (L.Z.)

* Correspondence: chenglf@nwpu.edu.cn

Received: 5 July 2018; Accepted: 14 August 2018; Published: 22 August 2018

Abstract: The mechanical and dielectric properties of two types of amorphous silicon nitride (Si$_3$N$_4$) fibers prior to and following annealing at 800 °C were studied. The tensile strengths of the Si$_3$N$_4$ fiber bundles were measured using unidirectional tensile experimentation at room temperature, whereas the permittivity values were measured at 8.2–12.4 GHz using the waveguide method. The results demonstrated that the tensile strength and dielectric properties of Si$_3$N$_4$ fibers were correlated to the corresponding composition, microstructure, and intrinsic performance of electrical resistance. The Si$_3$N$_4$ fibers with a lower content of amorphous SiN$_x$O$_y$ presented an improved thermal stability, a higher tensile strength, a higher conductivity, and a significantly stable wave-transparent property. These were mainly attributed to the highly pure composition and decomposition of less amorphous SiN$_x$O$_y$.

Keywords: Si$_3$N$_4$ fiber; wave-transparent; thermal stability; mechanical properties; dielectric properties

1. Introduction

Radome [1,2], as an indispensable part of high-performance missile weapons, plays a vital role in the normal operation of these weapons. In order that the missile weapons function in harsh environments, the performance required for wave-transparent materials under high temperature is increasingly demanding [3–6]. Silicon nitride (Si$_3$N$_4$), which demonstrates high strength, good thermal shock resistance, wear resistance, outstanding oxidation resistance, and chemical stability characteristics, is increasingly studied and applied as a high-temperature structural ceramic [7–11]. In addition, Si$_3$N$_4$ ceramics possess a low dielectric constant and a high electrical resistivity, which are the preferred properties for the transmission and insulation of electromagnetic waves in high-temperature environments [12–16]. Furthermore, Si$_3$N$_4$ nanomaterials, another hotspot of research, have both the advantages of Si$_3$N$_4$ and nanomaterials, which could be used to prepare nanofluids possessing different properties than their solids [17,18]. The continuous Si$_3$N$_4$ ceramic fiber is a new type of high-performance ceramic fiber, developed on the basis of precursor-converted continuous SiC ceramic fibers [19–21]. As a type of Si$_3$N$_4$ material, it has a series of excellent properties, proving to be a popular reinforced material candidate for high-temperature wave-transparent ceramic matrix composites (CMCs) used in radomes [21,22].

Considering the Si$_3$N$_4$ fiber as a core reinforcement material for radomes, there are strict requirements to follow regarding the mechanical and dielectric properties. Ideally, low and stable dielectric constant (ε) and dielectric loss (tan δ) are required in addition to the necessary mechanical properties, generally with values not exceeding 4.0 and 0.01 [23,24], respectively. During preparation, the fiber composition can differ due to different conditions, which affect it directly, consequently
affecting the corresponding microscopic structure and performance [25,26]. In this study, two types of Si$_3$N$_4$ fibers were heat treated at 800 °C, while the composition, microstructure, tensile strength, complex permittivity ($\varepsilon_j = \varepsilon' - \varepsilon''$), and dielectric loss ($\tan \delta = \varepsilon''/\varepsilon'$) of both Si$_3$N$_4$ fibers, in the as-received and heat-treated states, were investigated in detail.

2. Experimentation

2.1. Materials and Heat Treatments

The materials selected for experimentation were two different types of Si$_3$N$_4$ fiber bundles, supplied by Xiamen University of China, each consisting of 500 filaments, and woven into two-dimensional cloths by the Shaanxi Institute of Textile Science. The as-received Si$_3$N$_4$ fibers were produced by the pyrolysis of polycarbosilane (PCS). Because of the different pyrolysis conditions during preparation, the test results showed that the most significant difference between the two types of fibers was the oxygen content. For the convenience of subsequent description, the Si$_3$N$_4$ fiber with the relatively low oxygen content of 3.56 wt % (determined by a CONS elemental analyzer) was termed as Si$_3$N$_4$ fiber-L; the Si$_3$N$_4$ fiber with the relatively high oxygen content of 13.56 wt %, corresponded to Si$_3$N$_4$ fiber-H. In order to analyze the preparation temperature of the composites toughened by the Si$_3$N$_4$ fibers to see whether it had an effect on the characteristic performance of the fibers, the Si$_3$N$_4$ fibers and fiber cloths were placed in a furnace for chemical vapor decomposition (CVD) without gas at the temperature of 800 °C for up to 2 h of heat treatment, to simulate the preparation environment [27].

2.2. Microstructure Characterization

The surface and cross-section morphology of the Si$_3$N$_4$ fibers were analyzed using scanning electron microscopy (SEM) (S4700, Hitachi, Tokyo, Japan). The phase compositions of the Si$_3$N$_4$ fibers were analyzed using X-ray diffraction (XRD) (X’ Pert Pro, Philips, Amsterdam, The Netherlands) with Cu Kα ($\lambda = 1.54$ Å) radiation. The surface composition and chemical bonding states of the Si$_3$N$_4$ fibers were measured using X-ray photoelectron spectroscopy (XPS) (Axis Ultra, Oxford, UK). The fiber microstructure and crystalline state were accurately described using transmission electron microscopy (TEM) (G-20, FEI-Tecnai, Hillsboro, OR, USA). The heat treatment behavior of the as-received fibers was determined using thermogravimetric (TG) and differential scanning calorimeter (DSC) analysis (STA 449C, Selb, Germany) under Ar atmosphere at the heating rate of 10 °C/min to a maximum of 800 °C.

2.3. Property Characterization

The unidirectional tensile strengths at room temperature of the fiber bundles were tested. The two ends of the bundles were fixed on a steel plate with an adhesive of 50 mm in gauge length and of 0.2 mm/min in cross-head draw speed. This process was sufficiently slow, to simulate a quasi-static loading. Figure 1 presents the schematic illustration of a tensile specimen for single fiber bundles.
The electrical resistance of fiber bundles was tested with DC sources (6220, Keithley, Cleveland, OH, USA). Silver paste was added as coating on both ends of the fiber bundles to ensure a good electrical contact. The voltage values were determined by the corresponding current values, whereas the average value of resistance \( R \) was obtained using Ohm’s law. The average resistivity of each bundle of fibers \( \mu \) was calculated through the following equation:

\[
\mu = \frac{RS}{l},
\]

where \( S \) and \( l \) are the cross-sectional area and length of the fiber bundles, respectively. The relative complex permittivity testing of Si\(_3\)N\(_4\) fibers was conducted using a vector network analyzer (VNA) (MS4644A, Anritsu, Atsugi, Japan), with the waveguide method in the frequency band of 8.2–12.4 GHz. To ensure that the Si\(_3\)N\(_4\) fibers could be fixed to facilitate the measurement of dielectric property, the Si\(_3\)N\(_4\) fabrics, produced from Si\(_3\)N\(_4\) fiber-L and Si\(_3\)N\(_4\) fiber-H, were respectively composited with epoxy resin (68 vol %) to obtain fiber/resin composites (named as samples 1 and 2, respectively). To prevent the corresponding effects on the conductivity and dielectric properties, the surface sizing agents on both types of original Si\(_3\)N\(_4\) fibers were first removed by water soaking at 80 °C for a period longer than 0.5 h.

3. Results and Discussion

3.1. Microstructure and Composition of As-Received Fibers

Table 1 presents the fundamental characteristics of the Si\(_3\)N\(_4\) fibers. The O and C contents of the Si\(_3\)N\(_4\) fiber-H were higher, whereas the corresponding mechanical properties were closer to the precursor state [28].

| Materials       | Element/wt % | Diameter/µm |
|-----------------|--------------|-------------|
|                 | Si    | N    | O    | C    |       |
| Si\(_3\)N\(_4\) fiber-L | 59.79 | 36.0 | 3.56 | 0.65 | 12.2  |
| Si\(_3\)N\(_4\) fiber-H  | 52.39 | 33.14| 13.56| 0.91 | 13    |

Figure 2 presents the surface morphology and element mapping of both desized Si\(_3\)N\(_4\) fibers. The surfaces of both fibers (see Figure 2a,b) were smooth and flat without apparent defects, with no distinct difference between them. It was observed that both fibers displayed relatively uniform diameters of approximately 12.2 µm and 13 µm, respectively. The element mapping (see Figure 2c–f) presented the uniform distributions of Si, N, O, and C.

![Figure 2](image-url)
Figure 2. (a) Surface SEM images of Si$_3$N$_4$ fiber-L and (b) Si$_3$N$_4$ fiber-H, (c,d) scanning electron microscopy and energy dispersive pectroscopy (SEM-EDS) element mapping of Si$_3$N$_4$ fiber-L and (e,f) Si$_3$N$_4$ fiber-H.

The crystalline states of the untreated fibers and the heat-treated fibers at 800 °C are presented in Figure 3. No apparent crystal absorption peak were noted and only two broad diffraction peaks at approximately 23° and 69° were found in the typical XRD patterns of the two Si$_3$N$_4$ fibers annealed at 800 °C under vacuum. This revealed that the heat-treated fibers at 800 °C did not reach the crystallization temperature, remaining in the original amorphous state. High-resolution transmission electron microscopy (HR-TEM) combined with selected-area electron diffraction (SAED) were used to observe the detailed microstructures of both untreated Si$_3$N$_4$ fibers.
The XPS analyses of both desized fibers were performed to determine the corresponding surface composition and chemical bonding state. In the survey XPS spectra, presented in Figure 4a, the Si 2s, Si 2p, N 1s, C 1s and O 1s peaks were detected. As presented in Figure 4b, two peaks existed in the Si 2p spectrum: one peak was located at 101.8 eV and could be attributed to the Si–O bonds in the SiOx and SiNxOy phases, whereas the other peak was located at 101.2 eV, due to Si3N4, where the Si–O bond occupied a higher proportion on the Si3N4 fiber-H surface compared to the Si3N4 fiber-L. Similarly, two peaks existed in the N 1s spectrum, as presented in Figure 4c: one peak was located at 397.0 eV and could be attributed to the N–Si bond, whereas the other peak was located at 398.2 eV due to the N–Si–O bond, which was offered by the SiNxOy phase [29]. Furthermore, the O 1s spectrum presented in Figure 4d displayed two peaks. The lower energy peak was located at 532.9 eV, which corresponded well with the O–Si bond value. In addition, the higher energy peak located at 531.6 eV indicated the existence of COx at the fiber surface. At the Si3N4 fiber-H surface, a higher proportion of O–Si bond existed from the surface sizing agent on the fibers. Considering the existence of NH3 in the fiber preparation environment, the possibility of a SiNxOy phase is much higher than that of a SiOx one, following Reactions (2) and (3) [30]. Based on the latter analysis, it could be concluded that the two fibers were mainly composed of amorphous Si3N4, with low amounts of SiOx and SiNxOy phases.

\[
\text{SiO}_2(\text{s}) + \text{H}_2(\text{g}) = \text{SiO}(\text{g}) + \text{H}_2\text{O}(\text{g}), \quad (2)
\]

\[
\text{SiO}(\text{g}) + \text{NH}_3(\text{g}) = \text{SiN}_x\text{O}_y(\text{g}) + \text{H}_2\text{O}(\text{g}) + \text{H}_2(\text{g}), \quad (3)
\]
3.2. Effects of Heat Treatment on Microstructure and Composition

The element content of both Si$_3$N$_4$ fibers following annealing are presented in Table 2. Compared with Table 1, the mass percentage of N elements in both fibers decreased significantly after heat treatment, which may be due to the SiN$_x$O$_y$ phase decomposition, following Reaction (4) [31].

$$\text{SiN}_x\text{O}_y(s) = \text{SiO}(g) + \text{N}_2(g),$$  

Table 2. Elemental analysis of Si$_3$N$_4$ fibers following annealing.

| Materials       | Element/wt % |
|-----------------|--------------|
|                 | Si | N  | O  | C  |
| Si$_3$N$_4$ fiber-L | 66.97 | 27.23 | 5.12 | 0.68 |
| Si$_3$N$_4$ fiber-H | 64.26 | 25.68 | 9.24 | 0.82 |

The TG-DSC plots of the two as-received fibers are presented in Figure 5. For both fibers, endothermic peaks appeared at approximately 561 °C along with a weight decrease prior to reaching that temperature, which corresponded to the sizing agent decompositions on the fiber surfaces. Adversely, the heat flow curve significantly dropped at approximately 750 °C and its quality had a downward trend for the Si$_3$N$_4$ fiber-H. This meant that another endothermic reaction would start to occur, which could be associated with the SiN$_x$O$_y$ phase decomposition. Because of the negligible content during the SiN$_x$O$_y$ phase, the SiN$_x$O$_y$ decomposition caused almost no impact on the Si$_3$N$_4$ fiber-L.
The surface and cross-section morphology (insets) of the two types of desized fibers prior to and following heat treatment are presented in Figure 6, respectively. It was clear that the effect of heat treatment at 800 °C on the microstructure could be observed. Following heat treatment, the surfaces of both fibers changed from smooth and flat to rough. This occurred mainly due to the SiN$_x$O$_y$ decomposition, affecting the fibers’ performances. Moreover, a typical brittle fracture model could be observed from the cross-section morphology. The characteristic mirror, mist, and hackle features were clearly evident in these micrographs [32]. From the crack propagation path, it was observed that the crack source was mainly from the surface flaws for the heat-treated fibers.

In order to verify the SiN$_x$O$_y$ phase decomposition at the Si$_3$N$_4$ fiber-H surface, the corresponding surface chemical bonding states prior to and following annealing were analyzed using XPS. The (a) survey XPS spectra, (b) Si 2p, and (c) N 1s core level spectra are presented in Figure 7. Compared to
XPS spectra, (b) Si 2p, and (c) N 1s core level spectra are presented in Figure 7. Compared to the initial Si$_3$N$_4$ fiber-H, it was clear that the ratio of Si–O bond to Si–N bond had almost no change following annealing. This occurred because the heat treatment at 800 °C had little effect on the SiO$_x$ phase. In contrast, the N–Si–O bond had a significant reduction following annealing, as the main reason for the amount increase in surface defects, which proved the SiN$_x$O$_y$ phase decomposition.

Figure 7. (a) XPS survey spectra, (b) Si 2p, and (c) N 1s core level spectra recorded from Si$_3$N$_4$ fiber-H prior to and following annealing.

3.3. Effect of Heat Treatment on Room-Temperature Tensile Strength

The tensile strengths of fibers were measured using the fiber bundle tensile strength measurements. The corresponding dispersions could be well described using the Weibull distribution with two parameters [29]. Figure 8 presents the typical experimental load-displacement curve of the fiber bundles. Figure 8 shows that the fiber bundles were elastically deformed before breaking and that the elastic modulus was constant. Almost all filaments followed a simultaneous fracture behavior when the load reached its maximum, proving that the fiber bundle testing was reasonable. Moreover, a drop point and a post-failure “tail” region were noted. The former was the shake result of the testing equipment, whereas the latter occurred due to friction among neighboring filaments failing at different relative positions. These were not considered for the Weibull parameter calculation in this paper [33].
Figure 8. Typical experimental load-displacement curve of the fiber bundles, presenting simultaneous fracture behaviors.

The two-parameter Weibull function is given as follows [34]:

\[
F = 1 - \exp[- \left( \frac{\sigma_i}{\sigma_0} \right)^m],
\]

where \( F \) is the fracture probability of the fiber under a uniaxial tensile stress \( \sigma_i \), which is defined as fracture strength. \( \sigma_0 \) and \( m \) are the Weibull scale parameter and the Weibull modulus, respectively. As the value of \( m \) becomes higher, the strength distribution range becomes narrower and the function curve becomes steeper. Both depend only on the value of \( m \).

The following formula can be obtained, after taking two times the logarithm of Equation (5):

\[
\ln\ln\left(\frac{1}{1 - S}\right) = m \ln \sigma_i - m \ln \sigma_0,
\]

where \( S \) is the fracture probability from experiments and can be defined according to Equation (7):

\[
S_i = \frac{i - 0.5}{n},
\]

where \( n \) is the sample number and \( i \) is the rank of \( \sigma_i \). When the sample size was approximately 10, the \( S_i \) was in a weighted analysis [35]. It was apparent that the \( \ln\ln(1/(1 - S)) \) and \( \ln\sigma_i \) had a linear correlation, in which the slope was equal to \( m \) and the intercept of \( \ln\ln(1/(1 - S)) \) axis was equal to \( -m\ln\sigma_0 \). Therefore, the values of \( m \) and \( \sigma_0 \) could be derived from the experimental data and graphical relationships between \( \ln\ln(1/(1 - S)) \) and \( \ln\sigma_i \).

Table 3 lists the Weibull statistics and tensile strength of the two types of Si$_3$N$_4$ fiber bundles annealed under vacuum.

Table 3. Comparisons of Weibull statistics and tensile strength of two Si$_3$N$_4$ fiber bundles annealed under vacuum.

| Materials         | Temperature/°C | Weibull Modulus | Scale Parameter/MPa | Tensile Strength/MPa |
|-------------------|----------------|-----------------|---------------------|----------------------|
| Si$_3$N$_4$ fiber-L | as-received    | 17.80           | 1137.9              | 1104.4               |
|                   | 800            | 13.31           | 1142.2              | 1098.7               |
| Si$_3$N$_4$ fiber-H | as-received    | 13.92           | 866.8               | 835.0                |
|                   | 800            | 13.45           | 663.1               | 638.0                |
Figure 9 presents the linear fitting of the relationship between $\ln(1/(1 - F))$ and $\ln \sigma_i$ of the two Si$_3$N$_4$ fiber bundles. It was clear that the Weibull plots were evenly distributed on both sides of the fitted line, which indicated that the tensile strengths of the fiber bundles followed the two-parameter Weibull distribution.

Figure 10 presents the tensile test results combined with Table 3 and Figure 9. For the as-received fibers, the Si$_3$N$_4$ fiber-L strength was 1104.4 MPa, exceeding the 825 MPa reached by the Si$_3$N$_4$ fiber-H. In addition, compared to the Si$_3$N$_4$ fiber-H, the Si$_3$N$_4$ fiber-L had a higher Weibull modulus, which might be attributed to the neater arrangement and fewer internal flaws of filaments, where more filaments could evenly bear load and fracture at the same time, leading to higher strength and more centralized data. Following annealing at 800 °C under vacuum, the strength retention rate of the Si$_3$N$_4$ fiber-L was almost 100%, proving that the heat treatment at 800 °C had no effect on its structure, while the value of $m$ decreased from 17.8 to 13.31. This occurred because the fiber bundles scattered and the filaments could be uniformly loaded, mainly due to the sizing agent removal on the fiber surface. The tensile experimentation results demonstrated that the Si$_3$N$_4$ fiber-L following heat treatment at 800 °C could still maintain good tensile properties. Adversely, the Si$_3$N$_4$ fiber-H tensile strength decreased from 835 MPa to 638 MPa, while the value of $m$ was almost constant following heat treatment, demonstrating that the filaments of the as-received Si$_3$N$_4$ fiber-H had a high dispersion by nature. The strength retention result of only 76% indicated that the heat treatment at 800 °C caused damage due to the SiNxOy phase decomposition, resulting in a roughened and more defective surface of the Si$_3$N$_4$ fiber-H microstructure. This was consistent with the information presented in Figure 6.
According to the research by Taylor [32], a relationship exists among the different diameters of fibers and their strength. As mentioned above, the Si₃N₄ fiber-H diameter was higher. Because of the size effect, the probability of existing defects in the Si₃N₄ fiber-H was higher, which led to a lower and more dispersive strength. Furthermore, a higher content of SiNₓOᵧ phase was noted, resulting from the Si₃N₄ fiber-H impurities, which were unstable and would be destroyed, while bringing flaws and reducing performance at a high temperature. These could be indirectly proved from Figure 6, demonstrating that the Si₃N₄ fiber-L had improved mechanical properties and high thermal stability.

3.4. Effect of Heat Treatment on Room-Temperature Dielectric Properties

In addition to mechanical properties, the complex permittivity (ε = ε’ − jε”) is also an important performance parameter for wave-transparent applications. Figure 11 presents the real part (ε’) of permittivity, the imaginary part (ε”) of permittivity, and the dielectric loss (tan δ) of samples 1 and 2 as a function of frequency prior to and following annealing at 800 °C. The ε’, ε” and tan δ at 10 GHz of sample 1 were 3.43, 0.12, and 3.6 × 10⁻², respectively; for sample 2, the corresponding values were 3.18, 0.19, and 5.9 × 10⁻², respectively. Following annealing at 800 °C, these results became 3.19, 0.03, and 9.6 × 10⁻² for sample 1, respectively, whereas for sample 2, these results became 2.76, 0.16, and 5.6 × 10⁻², respectively. The fiber/resin composites displayed a low increase of ε’ and ε” compared to the epoxy resin (ε’ resin = 2.72, ε” resin = 0.07), due to the conductive behaviors of the Si₃N₄ fibers. The permittivity of the fiber/resin composites, especially for Si₃N₄ fiber-H, presented an apparent frequency dependence, which was one of the features of a dielectric material [36].

![Figure 11. Dielectric properties of two fiber/resin composites in X-band, prior to and following annealing.](image)

It is known that the real part of permittivity is related to the polarization effects and that the imaginary part is related to the electrical conductivity [25,37]. In the Si₃N₄ fiber, the Si₃N₄ was a polar molecule, becoming the dipole under an applied electric field. Under that field, the dipolar polarized and the dipolar polarization was a relaxation, presenting long relaxation time and attenuating high
amount of energy [24]. The Si$_3$N$_4$ fiber-L with a higher content of Si$_3$N$_4$ had a higher $\varepsilon'$, which implied that it possessed a stronger polarization ability.

For dielectric materials, the electrical conductivity ($\sigma$) is related to its dielectric property, which can be evaluated through the following equation [38]:

$$\sigma \varepsilon''(\omega) = \omega \varepsilon_0 \varepsilon''(\omega), \quad (8)$$

where $\sigma$ is the electrical conductivity, $\varepsilon_0$ is the free space permittivity ($\varepsilon_0 = 8.854 \times 10^{-12}$ F/m), and $\omega$ is the angular frequency. The resistivity and conductivity values of both fibers, prior to and following annealing, are presented in Table 4. Compared to the Si$_3$N$_4$ fiber-L, the Si$_3$N$_4$ fiber-H had a higher conductivity, which might be attributed to the highly electrical conductive phase of SiN$_x$O$_y$ compared to the Si$_3$N$_4$. The relationships between the imaginary part and conductivity of two Si$_3$N$_4$ fibers corresponded reasonably with Equation (6). It is known that the dielectric constant and dielectric loss decrease as the porosity increases [39]. This was caused by the SiN$_x$O$_y$ decomposition following annealing at 800 °C. Consequently, both fibers annealed at 800 °C had lower dielectric constant and dielectric loss compared to the as-received fibers.

Table 4. Resistivity and conductivity of two fibers prior to and following annealing.

| Materials       | As-Received $\mu\Omega$ m | As-Received $\sigma$/S m$^{-1}$ | Following Annealing $\mu\Omega$ m | Following Annealing $\sigma$/S m$^{-1}$ |
|-----------------|---------------------------|---------------------------------|----------------------------------|-------------------------------------|
| Si$_3$N$_4$ fiber-L | 18.94                     | 0.0528                          | 24.29                            | 0.0412                             |
| Si$_3$N$_4$ fiber-H | 31.17                     | 0.0321                          | 33.39                            | 0.0299                             |

4. Conclusions

For the two types of Si$_3$N$_4$ fibers studied in this work, the microstructure, the mechanical properties and the dielectric properties were investigated prior to and following heat treatment at 800 °C under vacuum. The microstructural analysis demonstrated that both fibers consisted of amorphous Si$_3$N$_4$, as well as SiO$_x$ and SiN$_x$O$_y$ phases. In addition, the Si$_3$N$_4$ fiber-H possessed a higher amount of SiN$_x$O$_y$ phase. Compared to the Si$_3$N$_4$ fiber-H, the Si$_3$N$_4$ fiber-L had a higher tensile strength and an improved thermal stability, as a result of its purer component. Following heat treatment, apparent defects and porous surface structures were noted in the Si$_3$N$_4$ fiber-H, leading to degradation due to the amorphous SiN$_x$O$_y$ phase decomposition. Moreover, the Si$_3$N$_4$ fiber-L had a higher permittivity and conductivity, resulting in its better polarization ability. Furthermore, the complex permittivity decrease of the annealed Si$_3$N$_4$ fiber/epoxy composites was also related to the SiN$_x$O$_y$ decomposition. The relatively higher strength, the better thermal stability and the same excellent dielectric properties indicated that the Si$_3$N$_4$ fiber-L possessed a high serving life at a serving temperature of at least 800 °C. This work could also contribute to the coordination of different service requirements and preparation processes and the selection of high-temperature wave-transparent materials for a potential application in ceramic matrix composites in harsh environments.

Author Contributions: Conceptualization, L.C.; data curation, J.Z. and J.L.; formal analysis, J.Z. and F.Y.; funding acquisition, F.Y., L.C., Y.L., and L.Z.; investigation, X.C.

Funding: This research was funded by the Chinese National Foundation for Natural Sciences under Contracts (Grant No. 51632007) and the Nature Science Foundation of China (Grants: 51602258, 51672217, and 51472201).

Acknowledgments: The authors wish to thank Xiamen University for the supply of Si$_3$N$_4$ fibers used in experimentation presented in this paper.

Conflicts of Interest: The authors declare no conflict of interest.
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