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Processing and properties of unidirectional SiO_{2f}/SiO_2 composites

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Abstract

Unidirectional SiO_{2f}/SiO_2 composites were processed with pressureless sintering and hot-pressing, respectively. The influences of the sintering temperature, atmosphere and pre-treatment on the properties were studied. It was found that both higher sintering temperature and air atmosphere promoted the crystallization of the silica fiber, which results in degrading the fiber properties and thus restrained the enhancement of mechanical properties of SiO_{2f}/SiO_2 composites. Flexural strength of the fibrous composites sintered with hot-pressing was higher than that for pressureless sintering. The promoted mechanical properties were attributed to the pull-out of the fiber. The in situ formed pyrolytic carbon (PyC) layer on the fiber was beneficial to the properties of the fiber, however, detrimental to the dielectric properties.

Keywords: C. Dielectric properties; C. Mechanical properties; SiO_{2f}/SiO_2 composites; Microstructure

1. Introduction

Fused silica is a kind of very important ceramic material with extremely low thermal-conductivity, thermal expansion, excellent thermal-shock resistance and anti-ablation, which made it receive special attention in high-temperature structural materials field in the past decades [1,2]. However, low flexural strength, low fracture toughness and poor rain erosion resistance of fused silica have restrained its further application. For the purpose of improving its mechanical properties without deteriorating its high transparency for electromagnetic wave in wide band, extensive efforts have been made during the past years. High-purity silica fiber with excellent dielectric properties is considered the most attractive candidate reinforcement in the silica composite [1,2].

Previous work mainly concentrated on the effects of the addition of short-chopped silica fiber and/or Nextel fiber on the properties of silica matrix [3–5]. It was showed that the fracture work and the rain erosion resistance were enhanced. However, the uneven distribution of fibers resulted in density and elastic modulus variations in the same sample [3,4]. Besides, the addition of fiber did not improve the fracture toughness due to the strong bonding of the fiber/matrix (F/M) interface [3,5].

In the preparation of fiber reinforced ceramic composites, the aggregation of short-chopped fiber in the matrix can be overcome by the introduction of continuous fiber. In the present study, unidirectional continuous silica fiber was selected as the reinforcement of silica matrix. The influences of processing conditions, including sintering temperature, atmosphere on the microstructures, phase composition and mechanical properties of the fibrous composites were initially investigated. To evaluate the influence of the densification on the properties of the fibrous composites, mechanical pressure was applied. To study the F/M interface property on the microstructure and properties, a pyrolytic carbon (PyC) layer was introduced by the in situ pyrolysis of surface coupling agent of fiber at high temperature.

2. Experimental procedure

2.1. Raw materials

Silica powder was obtained by ball-milling cracked fused silica tube. The average size of silica powder was about 3.8 μm. The tensile strength of the commercial high-purity silica tows (≥99.95 wt.% SiO_2, Feilihua Silica Glass Co., Jingzhou, PR China) was 1.01 GPa. The fiber was 1.32 dtex and the diameter was 5–10 μm. The relative weight of the organic coupling agent (polytetrafluoroethylene) on the silica fiber was about 4%.

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2.2. Processing of the samples

The preforms were prepared by the infiltration of a slurry consisting of silica powder and organic additives into the continuous silica tows as described in detail elsewhere [6]. The fiber content of the preforms was about 40 vol.%. The preforms were then dried at about 120 °C. Part of the preforms were pressurelessly sintered in the temperature range of 1250–1400 °C in air or vacuum, respectively. The resultant samples were noted as PLSA and PLSV sample. Some preforms were unidirectionally hot-pressed under an applied stress of 20 MPa in the temperature range of 1250–1400 °C in vacuum (noted as HPV sample). The rest of the preforms was heat-treated at 650 °C in air for 0.5 h so as to remove the coupling agent on the fiber, and then hot-pressed at 1250 °C in air for 0.5 h under an applied mechanical stress of 20 MPa (noted as AHP sample). The PLSV and HPV samples were heat-treated at 400–500 °C for 0.5–1 h so as to remove the residual PyC before the testing of mechanical and dielectric properties. The preparation conditions of the samples are summarized in Table 1. For microstructure observation, cross-sections perpendicular to silica fiber of both AHP and HPV sample were polished and etched in 3 wt.% HF aqueous solution for about 30 s.

2.3. Characterization

The as-processed samples were cut parallel to the direction of fiber and then ground into bars of 3 mm × 4 mm × 36 mm. Flexural strength and tensile strain were measured by three-point bending method with a span length of 30 mm and crosshead speed of 0.5 mm min^{-1} using an Instron-1195 Universal machine. The fracture surface was observed by scanning electron microscope (SEM, Shimadzu EPMA-8705 QHII). The density of the samples was determined by the Archimedes principle. Microstructure of the AHP and HPV samples was observed by field emission scanning electron microscope (FESEM, JEOL-JSM-6700F). The phase composition in the composite was determined by transmission electron microscope (TEM, Model JEM-200CXJ) analysis. Dielectric properties of the composite (the sample size: 10 mm × 10 mm × 2.5 mm) were measured in the frequency range of 0.01–1.0 GHz by direct electric voltage–current technology using Agileng-4291B.

Table 1
Preparation of the fibrous composites under various conditions

Samples	Pre-treatment	Sintering conditions	Post-treatment
PLSA	–	PLS, 1300–1400 °C, 0.5 h, air	–
PLSV	–	PLS, 1250–1400 °C, 0.5 h, vacuum	400–500 °C, air
AHP	650 °C, air	20 MPa, 1250 °C, 0.5 h, vacuum	–
HPV	–	20 MPa, 1250 °C, 0.5 h, vacuum	400–500 °C, air

3. Results and discussion

3.1. Effect of sintering temperature and atmosphere

Fig. 1 shows the TEM image of PLSA sample sintered at 1350 °C for 0.5 h. The selected area electronic diffraction (SAED) analysis (Fig. 1(a)) shows the matrix remained amorphous, however, the regular SAED spots indicate the happening of the crystallization of silica fiber. The contrast between the areas, such as A and B areas at near the surface and the center of the silica fiber cross-section was obvious. It can be attributed to the significant formation of cristobalite in fiber surface at temperature higher than 1350 °C [7,8]. The sintering in air promoted the surface crystallization of silica fiber [9,10]. The local volume change induced by the formation of cristobalite near to the fiber surface resulted in the propagation of cracks from fiber surface to the center (see arrows in the figure). Also, the mismatch of the thermal-expansion coefficient (TEC) of the cristobalite and amorphous silica matrix resulted in the crack around the silica fiber in the matrix.

Fig. 2 shows typical fracture surfaces of both PLSV and PLSA samples sintered at 1300 and 1400 °C, respectively. For the PLSV samples, it is obvious that the fibers in the 1300 °C-sample exhibited typical pull-out behavior (Fig. 2(a)). When the sintering temperature increased up to 1400 °C, less pulled-out silica fibers were observed and the fracture surface of the composite was flat (Fig. 2(b)). For PLSA samples, when sintered at 1300 °C, the pull-out behavior was only observed in the intrabundle fibers (Fig. 2(c)). When the temperature increased up to 1400 °C, no pull-out fiber can be seen in the PLSA sample. Comparing PLSV with PLSA samples sintered at 1400 °C (Fig. 2(b, d)), though their fracture surface was

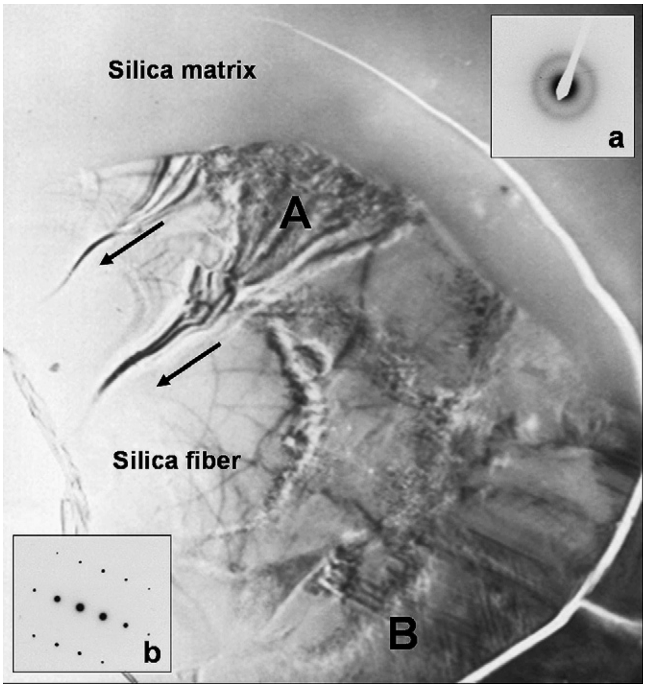

Fig. 1. TEM observation of the cross-section of PLSA sample processed at 1350 °C for 0.5 h.

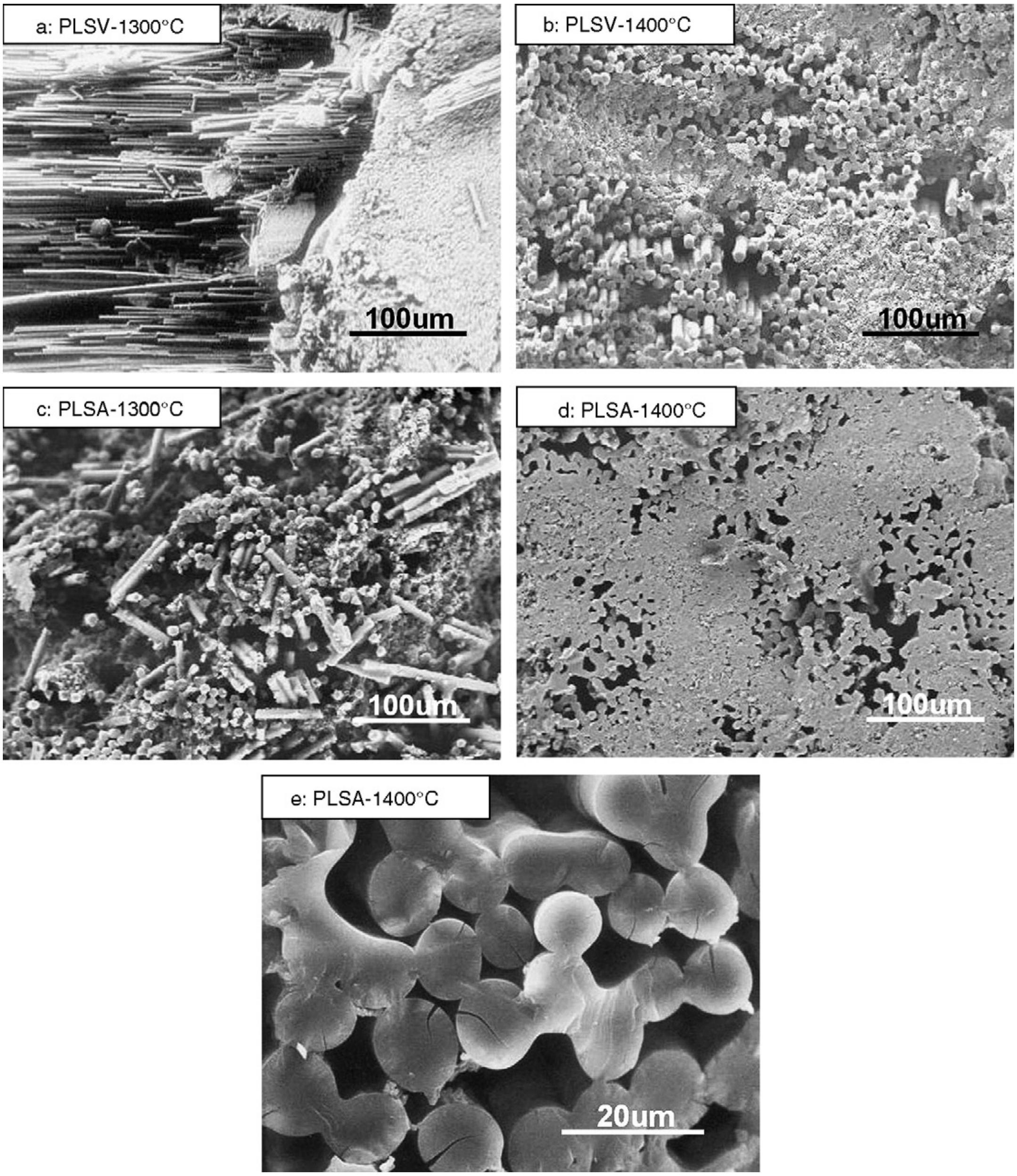

Fig. 2. Typical fracture surface of PLSV and PLSA samples sintered at 1300 and 1400 °C, respectively. (Upper-left: (a) PLSV-1300 °C, upper-right: (b) PLSV-1400 °C, down-left: (c) PLSA-1300 °C, down-right: (d) PLSA-1400 °C, down middle: (e) PLSA-1400 °C).

almost the same (flat), there were radial cracks from surface to the center in the fibers of the PLSA sample (see magnified image in Fig. 2(e)). From the cross-section of the fracture fiber, it can also be observed that the area near the surface was rough (Fig. 2(e)). It was attributed to the surface crystallization of the silica fiber, and these results are in accordance with that revealed in Fig. 1. Evidently, the increase of temperature accelerated the formation of cristobalite in the fiber no matter when the sample was sintered in air or in vacuum. In addition, at the same sintering temperature, the air promoted the cristobalite formation.

Fig. 3 shows the density and the flexural strength of the PLSed samples sintered at 1250–1400 °C. The density of PLSV sample increased linearly with the increasing temperature and reached 1.6 g cm^{-3} (the relative density is 72.7%) at 1400 °C. The flexural strength of both PLSV and PLSA samples increased to their maximum values (58.56 and 54.4 MPa, respectively) when the sintering temperature increased from 1250 to 1350 °C. The low flexural strength was attributed to the serious decline of fiber properties at elevated temperature. With the temperature increasing, both silica matrix and silica fiber softened and viscous flow occurred in the composites and the density of the composites was improved. The flexural strength was observed to be enhanced correspondingly. On the other hand, the retained strength of the fiber in fibrous composites after sintering plays key role to the flexural strength of fibrous composite. Comparing the microstructures shown in Fig. 2(a) and Fig. 2(b), more sintering-necks between fibers and/or powders can be observed. Obviously, higher sintering temperature promoted the crystallization of silica fiber and

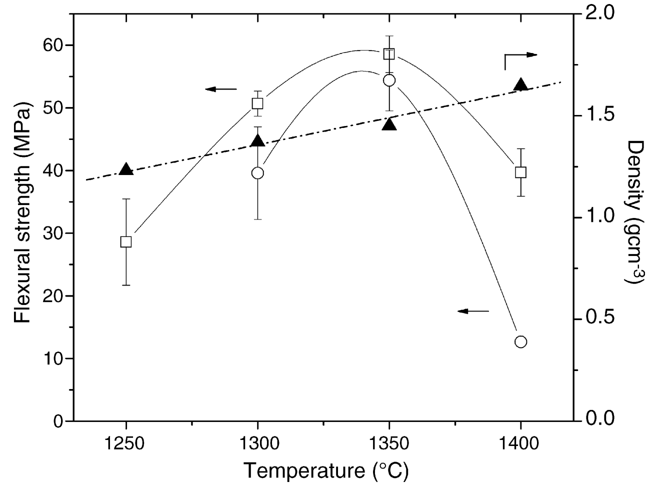

Fig. 3. Flexural strength of PLSV (□), PLSA (○) samples and density (▲) of PLSV sample sintered in the temperature range of 1250–1400 °C.

the mechanical properties of the fiber was degraded. Thus, the flexural strength of the PLSA sample decreased sharply at 1400 °C. Similar result happened in the case of PLSV sample. Besides, other factor such as oxidative atmosphere also contributed to the cristobalite formation [9,10]. So, the flexural strength of PLSA samples was lower than that of PLSV samples sintered in the whole temperature range of 1250–1400 °C.

Fig. 4 is typical load–displacement curves of the PLSed composites derived from the bending test. The highest point of the curve is correspondent with the flexural strength of the composites. The a, b and c curves demonstrated non-catastrophic fracture behavior of PLSV samples. With the rise of sintering temperature from 1250 to 1350 °C, the ultimate flexural strength increased due to the enhanced densification of the fibrous composites. For PLSA sample (curve d in Fig. 4), the ultimate flexural load was lower than that of the PLSV sample (curve c in Fig. 4) and the curve dropped sharply after the flexural load reached the maximum value. As discussed, both high temperature and air condition were favorable for the crystallization in silica fiber, which resulted in the mechanical properties degradation of PLSA sample. Similar results have been discussed on microstructure analysis.

3.2. Effect of pre-treatment and sintering methods

Hot-pressing is usually another more effective method to improve the properties of fibrous composites. Fig. 5 is the FESEM observation of the as-polished cross-sections of the samples prepared with pressure applied: AHP (Fig. 5(a)) sample and HPV (Fig. 5(b)) sample. Fig. 5(a) shows that almost no silica fiber can be observed from the cross-section of the AHP sample. This is because the coupling-agent on the fiber surface was removed by heat-treating the preform in air at 650 °C for 0.5 h before hot-pressing. That is, no residual PyC layer on the surface of the fiber. Therefore, the fibers were integrated to the silica matrix. However, the circinal crack revealed that there were few silica fibers remaining after the sintering process. Contrarily, Fig. 5(b) shows that there were many silica fibers remaining in the HPV sample. There is no pre-treating for the HPV sample. Thus, the in situ formed PyC layer during sintering prevented the fiber from integrating with the matrix.

Fig. 6 shows the results compared on the flexural strength of between the PLSV sample, AHP sample and HPV sample and

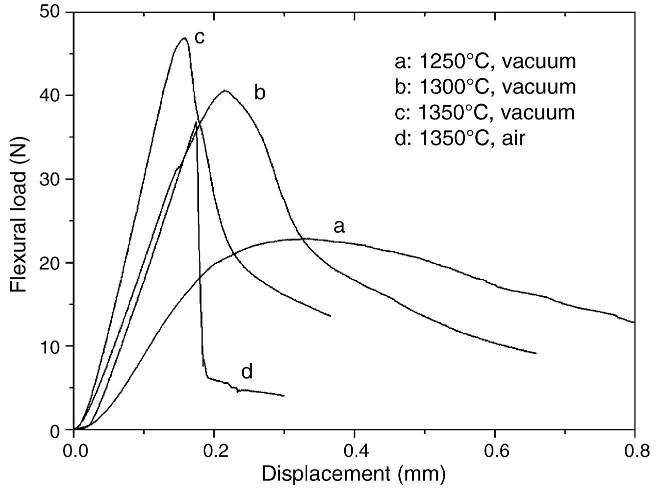

Fig. 4. Typical stress–strain curves from bending test for the composites PLSed under various conditions.

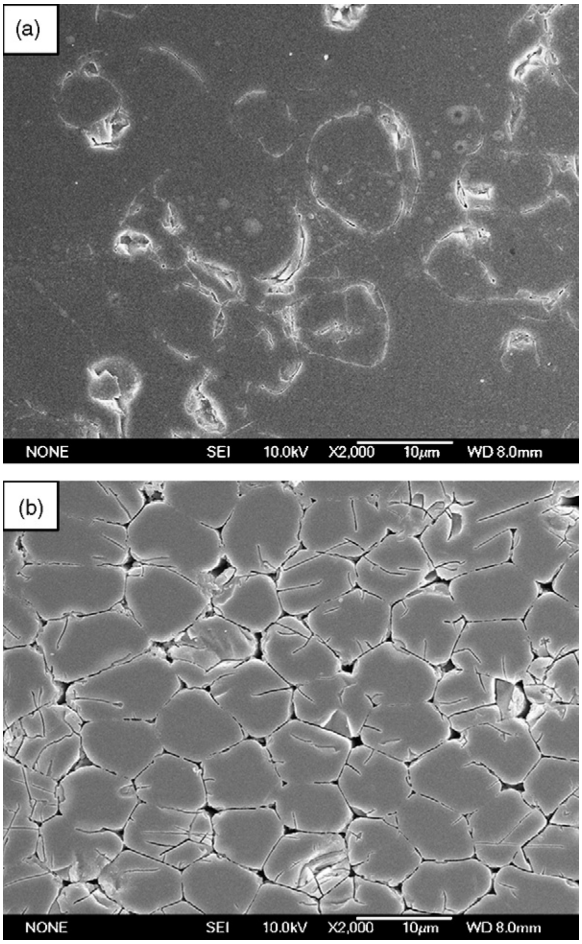

Fig. 5. Cross-sections (a) AHP and (b) HPV sintered at 1250 °C without and with PyC layer, respectively.

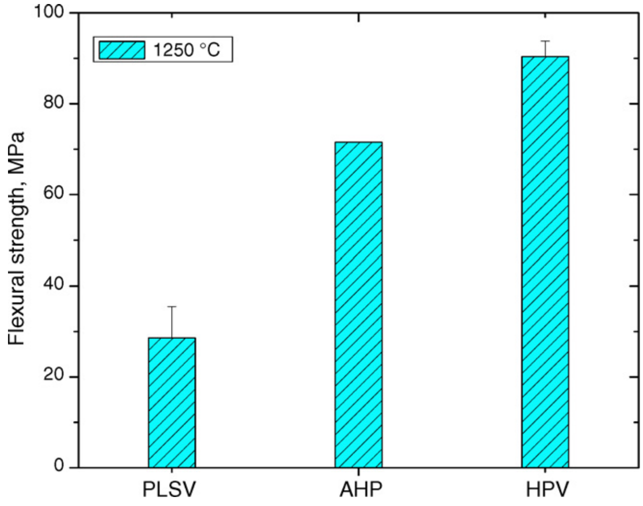

Fig. 6. Flexural strength of PLSV, AHP, and HPV samples sintered at 1250 °C.

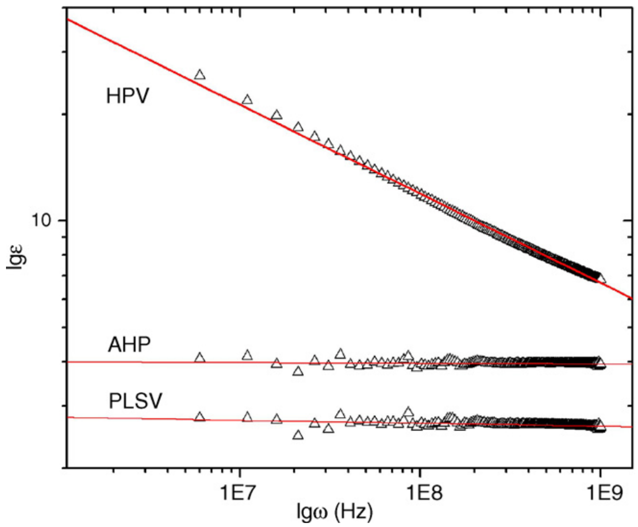

Fig. 7. lgε ~ lgω relationships of PLSV, AHP and HPV samples sintered at 1250 °C.

PLSV sample sintered at 1250 °C, respectively. It is obvious that the flexural strength of the hot-pressed samples (AHP and HPV) is higher than that for the PLSV sample. Furthermore, the flexural strength of HPV sample was higher than that of AHP sample. Comparing with the microstructures of AHP and HPV samples (as shown in Fig. 5), it is suggested that the in situ PyC layer not only retarded the amalgamation of silica fiber and silica matrix but also reduced the bonding strength between F/M interfaces (Fig. 6(b)). As a result, the flexural strength of the HPV sample was improved.

Fig. 7 shows the frequency dependency of dielectric properties of PLSA, AHP and HPV samples. According to Walton's function [11]: $\varepsilon_c = \varepsilon_0^{1-p}$, where, ε_c stands for the dielectric constant of the composites, ε_0 the dielectric constant of the full dense materials and p the porosity of the composites, the dielectric constant is determined by the relative density of the composites. For PLSV and AHP samples, which have had the carbon removed-off either before or after the sintering of the fibrous composites, the dielectric constant ε kept stable within the testing band (0.01–1.0 GHz). The ε values of PLSV and AHP samples were 2.60 and 3.95 (1.0 GHz), respectively, which was in agreement with the fact that the density of AHP sample was higher than that of PLSV sample. However, the in situ formed PyC interphase in the HPV sample cannot be removed-off. Thus, the dielectric property of the HPV sample was deteriorated. The ε value of the HPV sample varied linearly with frequency in the testing range.

4. Conclusions

(1) Continuous silica fiber is an effective reinforcement to the silica matrix. The fibrous composite with a flexural strength of 58.6 MPa and a density of 1.4 g cm^{-3} was obtained at 1350 °C in vacuum. On the other hand, higher processing temperature and oxygen atmosphere is favorable to the formation of cristobalite in silica fiber, which is detrimental to the mechanical properties.
(2) The flexural strength of the samples may be significantly improved by high pressure processing. The in situ formed PyC layer is positive to the enhancement of mechanical properties but negative to the dielectric properties.

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