3D C_f/SiBCN composites prepared by an improved polymer infiltration and pyrolysis

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Received: December 13, 2017; Revised: March 29, 2018; Accepted: April 25, 2018

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Abstract: Using liquid poly(methylvinyl)borosilazanes (PMVBSZ) as precursor, carbon fiber reinforced SiBCN matrix composites (C_f/SiBCN) were fabricated by a modified polymer infiltration and pyrolysis (PIP) process. With dicumyl peroxide added as cross-linking agent, the PMVBSZ could be solidified at a low temperature of 120 °C, leading to a high ceramic yield of ~70%. The cross-linking mechanism and ceramization processes of the precursor were investigated in detail. Moreover, a modified infiltration technology was developed, which improved the efficiency and protected the precursor against moist air during PIP. Consequently, the obtained C_f/SiBCN composites had an oxygen content of around 1.22 wt%. Benefiting from the high ceramic yield and high efficiency of the modified PIP, C_f/SiBCN composites with an open porosity of ~10% and uniform microstructure were obtained after only 7 cycles of PIP. The flexural strength and fracture toughness of the derived C_f/SiBCN composites were 371 MPa and 12.9 MPa·m^{1/2}, respectively. This work provides a potential route for the fabrication of high performance C_f/SiBCN composites.

Keywords: C_f/SiBCN; ceramic matrix composites (CMCs); polymer infiltration and pyrolysis (PIP); dicumyl peroxide (DCP)

1 Introduction

Silicoboron carbonitride (SiBCN) ceramics have attracted great attention due to their excellent thermal stability (up to 2000 °C) [1,2], high temperature mechanical

properties [3,4], resistance to oxidation [5], and creep at elevated temperatures [6]. These properties make the SiBCN ceramics receive wide publicity in recent decades, showing great potential for applications as high temperature structural and multifunctional heat resistant components in aerospace industry [7]. However, the application of SiBCN ceramics in these areas may be greatly limited due to their low toughness and poor thermal shock resistance [8,9]. Effective ways to

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strengthen them such as incorporation of fibers, whiskers, and/or particles are necessary [10]. Based on the successful application of continuous carbon fiber reinforced ceramic matrix composites, such as C_f/SiC [11], the composites prepared by introducing SiBCN ceramics into carbon fiber preforms (C_f/SiBCN) are supposed to have a wider application in a harsh environment, such as hypersonic aircraft thermal structures, advanced rocket propulsion thrust chamber, and other space system.

Generally, there are three mostly-applied methods for the fabrication of ceramic matrix composites, namely chemical vapor infiltration (CVI) [12], reactive melt infiltration (RMI) [13], and polymer infiltration and pyrolysis (PIP) [11]. However, due to the complexity in composition of SiBCN, it is very difficult to obtain SiBCN by CVI or RMI process. To the best knowledge of the authors, C_f/SiBCN composites have only been successfully fabricated by PIP process. Partially due to the difficulty in large-scale synthesis of proper SiBCN precursors, very limited results have been reported on the preparation of C_f/SiBCN composites by PIP. Weinmann *et al.* [14] fabricated C_f/SiBCN composites using a mixture consisted of oligovinylsilazane ($[(H_2=CH)SiH-NH]_n(OVS)$) and tris(methyldihydridosilyl)ethylene borane $B(C_2H_4Si(CH_3)H_2)_3$ as the precursors for SiBCN. Lee *et al.* [15] reported the obtained C_f/SiBCN composites based on above precursor have a relative density of 89% and an average bending strength of 255 MPa. Moreover, the introduction of SiC filler particulates into the matrix can further improve the thermal stability of C_f/SiBCN composites [16]. It was reported that the C_f/SiBCN composites with SiC filler particulates could retain 96% of its room-temperature strength and possess non-brittle fracture behavior even after heating at 1700 °C for 10 h in Ar. Using sodium borohydride as boron source, Zhao *et al.* [17] synthesized liquid soluble SiBCN ceramic precursor with a ceramic yield of 75.6% and a low viscosity of 65 mPa·s, which can efficiently prepare ceramic matrix composites.

Two disadvantages have been recognized for the fabrication of C_f/SiBCN composites via traditional PIP process. Firstly, high temperature (200 °C or even higher) and long time (30 h) are required for the cross-linking of conventional SiBCN precursor [15], which makes the long PIP fabrication period even longer. On the other side, the precursor for SiBCN is generally sensitive to air and moisture. However, the traditional PIP process cannot avoid direct contact

between the precursor and moist air, particularly during the long solidification period, which will degrade the performance of the C_f/SiBCN composites. To address the above two disadvantages, the present work developed a modified PIP process for the fabrication of high performance C_f/SiBCN composites. A commercially available poly(methylvinyl)borosilazanes (PMVBSZ) with active $-CH=CH_2$ groups was selected as the precursor for SiBCN. Dicumyl peroxide (DCP), which was used to cross-linking process for vinyl, allyl-containing polycarbosilanes, and polysilazanes [18,19], was added as cross-linking agent to lower the solidification temperature of the SiBCN precursor. On the other hand, a modified infiltration technology was developed to improve the efficiency and protect the precursor against moist air during PIP for the fabrication of C_f/SiBCN composites.

2 Experimental

A liquid poly(methylvinyl)borosilazanes (PMVBSZ, Institute of Chemistry, Chinese Academy of Sciences) was used as the precursor for SiBCN. Dicumyl peroxide (DCP, Sinopharm Chemical Reagent Co., Ltd.) was used as cross-linking agent for PMVBSZ. 3D needle-punched carbon fiber preforms fabricated with T300 carbon fiber (12K) were used as the reinforcements of the composites. The 3D fiber fabrics have a dimension of $L \times W \times H = 150 \text{ mm} \times 150 \text{ mm} \times 6 \text{ mm}$, and a density of 0.52 g/cm^3 with a fiber volume ratio of about 28%. Before PIP process, pyrolytic carbon (PyC) interphase with a thickness of 200–300 nm was deposited on the preforms by CVI.

To lower the cross-linking temperature and shorten the time, 1 wt% dicumyl peroxide (DCP) was added as cross-linking agent. The cross-linking process of PMVBSZ was carried out at 120 °C for 2 h. The cured bulk precursors were pyrolyzed at 1100 °C in Ar atmosphere for 2 h with a heating rate of 5 °C/min, and then cooled down to room temperature at 5 °C/min. For comparison, the cross-linking and pyrolysis process of PMVBSZ without DCP addition was also studied. To investigate the curing mechanism, the functional groups of PMVBSZ before and after cross-linking process were analyzed by a FT-IR spectrometer (Bruker Tensor 27, Germany). Liquid-state ^{13}C NMR of precursor was obtained by Bruker Advance III HD 500 MHz nuclear magnetic resonance spectrometer (Bruker Co., Germany)

operating at 125.77 MHz. Sample was dissolved in CDCl_3 solution. The chemical shift was referred to tetramethylsilane (TMS) as the external standard. The solid-state ^{13}C (^1H) cross-polarization magic angle spinning (CPMAS) NMR spectra of the precursor after cross-linking was performed on a Bruker DRX 400 NMR spectrometer (Bruker Co., Germany) operating at 150.78 MHz, using a 3.2 mm Bruker probe spinning frequency of 15.0 kHz and a ^1H spin-locking frequency of 15.0 kHz. In addition, ^{29}Si and ^{11}B MAS NMR spectra of SiBCN ceramics were also measured on a Bruker DRX 400 NMR spectrometer using the single pulse (SP) technique operating at 119.12 MHz for ^{29}Si and 192.37 MHz for ^{11}B . The sample was spun at 10.0 kHz using a 4.0 mm Bruker probe for solid-state ^{29}Si and ^{11}B . The chemical shift values are reported relative to TMS for ^{13}C and ^{29}Si ($\delta = 0$) or BF_3OEt_2 for ^{11}B . Thermogravimetric (TG) curves of cured PMVBSZ were determined on a STA 409/PC simultaneous thermal analyzer (Netzsch, Germany) with a heating rate of $10^\circ\text{C}/\text{min}$ in flowing Ar. The boron, carbon, nitrogen, and oxygen contents were determined by inductively coupled plasma (ICP), carbon analyzer CS2000, and Oxygen-Nitrogen analyzer. Phase composition of the specimens was analyzed using X-ray diffraction (XRD) with $\text{Cu K}\alpha$ radiation.

A modified infiltration technology (shown in Fig. 1) was developed for the PIP process. During infiltration process, the preforms were placed in a flexible container in vacuum. This method is expected to reduce the waste of precursor, improve the impregnation efficiency, and protect the precursor against air and moisture during infiltration and solidification. The preform impregnated the precursor was cured at 120°C

Fig. 1 Schematic diagram of modified infiltration technology.

for 2 h. After curing, composites were pyrolyzed at 1100°C for 2 h with a heating rate of $5^\circ\text{C}/\text{min}$ in Ar atmosphere. The procedure of impregnation, curing, and pyrolysis was repeated until the weight increase was less than 1%. In this work, 7 cycles were used.

Density and open porosity of the prepared 3D C_f/SiBCN composites were measured by the Archimedes method. Bending strength and elastic modulus of the final composites were characterized by a three-point bending test (DDL20, Changchun Research Institute for Mechanical Science Co., Ltd., Changchun, China) with a span length of 50 mm and a crosshead speed of 0.5 mm/min. The dimensions of the specimens for three-point bending test were $4\text{ mm} \times 6\text{ mm} \times 60\text{ mm}$. Tensile strength was also measured by DDL20 with a sample size of $4\text{ mm} \times 8\text{ mm} \times 100\text{ mm}$ and a crosshead speed of 0.5 mm/min. Fracture toughness was measured by a single edge notch beam (SENB) method, with a specimen size of $4\text{ mm} \times 8\text{ mm} \times 50\text{ mm}$, notch length of 4 mm, crosshead speed of 0.5 mm/min, and support span of 40 mm. For all the mechanical tests in this work, at least five specimens were tested to give the mean value. Microstructures of both the fracture surfaces and polished cross sections of the specimens were observed using a field-emission scanning electron microscope (Hitachi S-4800, Tokyo, Japan).

3 Results and discussion

3.1 Cross-linking process of PMVBSZ

Figure 2 shows the optical images of PMVBSZ after cross-linking at 120°C for 2 h. The precursor without DCP added is still liquid after heat treatment (Fig. 2(a)). With DCP added as cross-linking agent, the PMVBSZ becomes a transparent and foam-free solid (Fig. 2(b)). This reveals that DCP effectively promotes cross-linking of PMVBSZ.

FT-IR spectroscopy was used to study the cross-linking mechanism of the precursor. Figure 3(a) shows the FT-IR spectra of PMVBSZ with DCP added before and after cross-linking. The absorption bands of N–H at 3190 and 1170 cm^{-1} are observed in both spectra. The broad band between 1300 and 1500 cm^{-1} is attributed to overlap of B–N stretching at 1400 cm^{-1} and $-\text{CH}_2-$ bending vibration at 1350 cm^{-1} . The minor band at 790 cm^{-1} is ascribed to B–N bending vibration. The signal at 950 cm^{-1} belongs to Si–N–Si bond. Besides, the bands of Si–O–Si (1010 cm^{-1}) and Si–OH (530 cm^{-1})

Fig. 2 Optical images of PMVBSZ after treatment at 120 °C/2 h: (a) without DCP and (b) with DCP added.

Fig. 3 (a) FT-IR spectra and (b) ^{13}C NMR spectra before cross-linking and ^{13}C NMR spectra after cross-linking of PMVBSZ with DCP added.

appear, which may be due to the hydrolysis of Si-NH during testing in air. The absorption bands at 3047, 3006, and 1593 cm^{-1} are characteristic $=\text{CH}_2$, $=\text{CH}$, and $\text{C}=\text{C}$ stretching bands of vinyl group. The absorption bands at 2956 and 2899 cm^{-1} are assigned to $\text{C}-\text{H}$ stretching. The band at 1254 cm^{-1} originates from the stretching mode of $\text{Si}-\text{CH}_3$ bonds [20].

After cross-linking, the absorption peaks of $\text{Si}-\text{N}-\text{Si}$, $\text{N}-\text{H}$, and $\text{B}-\text{N}$ decrease slightly, which can be attributed to the reaction of $\text{N}-\text{H} + \text{CH}_2=\text{CH}- \rightarrow \text{N}-\text{CH}_2-\text{CH}_2-$ [21]. On the other hand, the absorption intensity of $=\text{CH}_2$, $=\text{CH}$, and $\text{C}=\text{C}$ stretching bands of vinyl group decreases sharply. Yu *et al.* [22] have reported semiquantitative calculation of the reaction degree of $\text{C}=\text{C}$, by assigning the intensity of $\text{Si}-\text{CH}_3$ at $\sim 1254 \text{ cm}^{-1}$ as the reference. And it was determined that the reaction degree of $\text{C}=\text{C}$ was $\sim 86\%$ during the cross-linking process, which demonstrates that the most

double bond of vinyl groups transformed into single bond during the cross-linking process.

Furthermore, liquid/solid-state NMR analyses were performed to investigate the structural transformation of PMVBSZ during cross-linking process. The liquid-state ^{13}C NMR spectrum of PMVBSZ before cross-linking and the solid-state ^{13}C (^1H) CP/MAS NMR spectrum of cross-linked product are shown in Fig. 3(b). The resonance at 2.84 ppm originates from $\text{Si}-\text{CH}_3$. The peaks at 131 and 141 ppm can be assigned to $\text{Si}-\text{CH}=\text{CH}_2$ (sp^2) [23], which become weaker after cross-linking. Moreover, a broad signal from 12 to 46 ppm appears after cross-linking, which can be attributed to $-\text{CH}_2-$ bridges (sp^3). The comparison of ^{13}C NMR spectra further confirms that partial vinyl groups are polymerized and form $-\text{CH}_2-$ bridges (sp^3) after cross-linking [24].

Based on the above analysis, the cross-linking process of PMVBSZ can be inferred from the group transformation, as shown in Eqs. (1)–(3). At first, DCP is decomposed and two cumyloxy free radicals ($\text{R}\cdot$) are released [25–27]. And then, the cumyloxy free radicals ($\text{R}\cdot$) will react with vinyl double bonds, generating macromolecular free radicals. The macromolecular free radicals will continue to react with other vinyl double bonds. With this process happening, more and more vinyl groups are polymerized and form $-\text{CH}_2-$ bridges (sp^3). Consequently, the precursor transforms from liquid to solid.

3.2 Polymer-to-ceramic conversion process of PMVBSZ

Without DCP added, the pyrolyzed product of PMVBSZ shows a loose foam morphology, as shown in Fig. 4. With DCP added, the pyrolyzed product is stiff, flat, and compact without obvious pores. The linear shrinkage of pyrolyzed product of PMVBSZ with DCP added is around 20%. To understand the pyrolysis process, TG analysis was performed, as shown in Fig. 4. With DCP added, the weight loss of PMVBSZ at 25–200 °C is negligible. The weight loss at 200–500 °C and 500–1000 °C is around 5% and 25%, respectively. The ceramic yield of the cross-linked product with DCP

Fig. 4 TG analysis of cross-linked PMVBSZ with and without DCP added. The insets are the optical images of corresponding pyrolyzed products.

added is as high as 70%. For the PMVBSZ without DCP added, it shows a sharp weight loss at 25–200 °C and a very low ceramic yield of around 15%. Based on the above results and analysis, DCP initiates polyaddition of vinyl groups at 120 °C, which increases the molecular weight of PMVBSZ and effectively reduces the evaporation of small molecules during pyrolysis, resulting in the ceramic yield of the precursor increasing from 15% to 70%.

The molecular structural evolution during the polymer-to-ceramic conversion process was studied by FT-IR, as shown in Fig. 5. As the temperature increases to 300 °C, the =CH₂, =CH, and C=C absorption bands at 3047, 3006, and 1593 cm⁻¹ almost disappear completely. After annealing at 500 °C, the intensity of the N–H, C–H, Si–CH₃, and Si–NH weakens significantly. At 700 °C, the absorption bands of C–H and Si–CH₃ almost disappear, which is attributed to the two-step radical reaction; the first step involves Si–C bond cleavage and is followed by the abstraction of a hydrogen atom from N–H or C–H bonds (Eq. (4)) [28–31]. The disappearance of the N–H and Si–NH bands indicates the completion of transamination reaction (Eq. (5)) [32,33]. Interestingly, the wide bands at about 1500 cm⁻¹ emerge,

Fig. 5 FT-IR spectra of cross-linked PMVBSZ pyrolyzed at different temperatures.

which could indicate the presence of amorphous carbon [30]. At temperatures higher than 900 °C, almost all the absorption peaks disappear, indicating that pyrolysis processes are completed and nearly no residual organics are existed.

The chemical compositions of PMVBSZ and SiBCN ceramics are listed in Table 1. As expected, the main constituents of the as-prepared SiBCN ceramics are Si, C, N, and B. The oxygen impurity content of the sample is around 1.22%, which is close to the oxygen content of SiBCN ceramics fabricated by standard Schlenk techniques [34]. Therefore, the modified PIP process exhibits certain advantages in maintaining the low oxygen contentment of SiBCN ceramics.

XRD was performed to analyze crystallinity of the as-prepared SiBCN ceramics. As shown in Fig. 6(a), no obvious diffraction peaks can be detected, indicating that the SiBCN ceramics are amorphous. To further determine the bonding structure of SiBCN, ²⁹Si spectra and ¹¹B NMR spectra of the obtained SiBCN ceramics were analyzed. ²⁹Si spectrum of SiBCN ceramics is shown in Fig. 6(b). The spectrum includes a peak at −33 ppm with a broad shoulder near −18 ppm, corresponding to SiCN₃ and SiC₄ structural units, respectively. The peak at about −50 ppm is attributed to the SiN₄ tetrahedral structure [35]. This covers the chemical shift ranged from 0 to −70 ppm, corresponding to the presence of mixed bonded SiC_xN_{4−x} tetrahedra with 0 ≤

Table 1 Chemical composition of PMBSZ and SiBCN ceramics

	Si	B	C	N	O
PMVBSZ (wt%)	37.20	2.51	39.95	18.30	2.04
SiBCN (wt%)	51.34	3.36	24.98	19.10	1.22

Fig. 6 (a) XRD pattern, (b) ^{29}Si MAS NMR spectrum, and (c) ^{11}B MAS NMR spectra of SiBCN ceramics pyrolyzed at 1100 °C.

$x \leq 4$ [34–38]. Figure 6(c) shows the ^{11}B spectra of the as-obtained SiBCN ceramics. The ^{11}B spectra display a broad resonance in the range of 10–50 ppm, revealing the presence of BN_3 (25–30 ppm) and BN_2C (30–35 ppm) [34,37,39,40].

Therefore, it can be concluded that the molecular structure of the as-obtained amorphous SiBCN is characterized by mixed bonding in the form of $\text{SiC}_x\text{N}_{4-x}$ ($0 \leq x \leq 4$) tetrahedral units and $\text{BC}_x\text{N}_{3-x}$ ($0 \leq x \leq 1$) triangles. Widgeon *et al.* [34,35,37,38] have assumed that SiBCN contains SiCN and BCN nanodomains with core-shell structures. The cores of these nanodomains are enriched in SiN_4 tetrahedra and BN_3 triangles, while the shells are primarily composed of SiC_4 tetrahedra and BCN_2 triangles. The BNC domain occupies the interfacial region and separates the SiCN and C domains.

3.3 Fabrication and properties of C_f/SiBCN composites by modified PIP

Based on the above investigation on cross-linking, pyrolysis process of PMVBSZ, as well as the analysis on molecular structure of the as-obtained SiBCN, carbon fiber reinforced SiBCN composites (C_f/SiBCN) were fabricated by a modified PIP process. As shown in Fig. 1, precursor can be protected against air and moisture during infiltration and solidification in the modified PIP processing. Figure 7(a) shows the weight increase of C_f/SiBCN composites as a function of the number of PIP cycles. Weight increase is around 65.38% at the first PIP cycle. The total weight increase is around 161.76% after 7 cycles. At the 7th cycle, the weight increase is lower than 1% and the PIP process was stopped then. As reported before, more than 16 cycles are generally needed for fabrication of C_f/SiBCN composites by the conventional PIP process [15]. Therefore, the modified PIP process used in this work shows very high densification efficiency. The high PIP efficiency in this work can be ascribed to several reasons, including: high ceramic yield of PMVBSZ, low viscosity (6.2 mPa·s) of PMVBSZ, as well as advantages of the modified infiltration technology. The low viscosity of PMVBSZ allows the precursor to fill in the blanks of preform sufficiently, while the modified infiltration technology can avoid the precursor outflowing

Fig. 7 (a) Weight increase and (b) density and open porosity of C_f/SiBCN composites as a function of the number of PIP cycles.

from the preform before cross-linking. Density and open porosity evolution of C_f/SiBCN composites during PIP process is shown in Fig. 7(b). After 7 cycles, the density and open porosity of the C_f/SiBCN composites are 1.734 g/cm³ and 10.3% respectively. By contrast, Lee *et al.* [15] took 16 cycles to achieve the relative density of ~90% for C_f/SiBCN composites by conventional PIP process.

Figures 8(a)–8(c) show the SEM images of polished cross sections of the as-fabricated C_f/SiBCN composites. The C_f/SiBCN composites show a highly dense microstructure, although some pores still exist in the composites. Figure 8(c) offers a more detailed microstructure of the composites. It can be observed that thickness of the PyC interface is around 250 nm, which is combined with the fiber and SiBCN matrix closely. As discussed above, the high densification of the composites can be attributed to its low viscosity and high ceramic yield of PMVBSZ, as well as the advantages of the modified infiltration technology. As shown in Fig. 4, cross-linked PMVBSZ converted into a large dense matrix with few cracks after pyrolysis, where the cracks can be easily filled in the following PIP cycles. This leads to a strong bonding strength of the matrix, which

implies a high load-transfer capacity and low crack initiation probability of the composites.

The phase composition of SiBCN ceramics, carbon fiber, and C_f/SiBCN composite were determined by X-ray diffraction. As shown in Fig. 8(d), two peaks at 26° and 43° are observed in carbon fiber and C_f/SiBCN composites, which can be attributed to the graphitic (002) plane and (101) plane, respectively, corresponding to the carbon fiber [41]. In addition, no other diffraction peaks are detected in C_f/SiBCN composite, indicating that the SiBCN matrix is amorphous.

Table 2 shows the measured mechanical properties of the C_f/SiBCN composites. Flexural strength, elastic modulus, tensile strength, and fracture toughness of the C_f/SiBCN composites are 371 MPa, 32 GPa, 188 MPa, and 12.9 MPa·m^{1/2}, respectively. Compared with the C_f/SiBCN composites fabricated via conventional PIP process by 16 cycles, bending strength of the C_f/SiBCN composites fabricated in this work is improved by ~45% (255 MPa in Ref. [15]). Therefore, the modified PIP process proposed in this work has demonstrated certain superiority, showing improved densification efficiency and mechanical properties. Figure 9(a) shows the bending stress–strain curve of the C_f/SiBCN composites,

Fig. 8 (a)–(c) SEM images and (d) XRD patterns of the polished cross sections of SiBCN ceramics, C fiber, and C_f/SiBCN composites.

Table 2 Mechanical properties of the C_f/SiBCN composites

	Flexural strength (MPa)	Elastic modulus (GPa)	Tensile strength (MPa)	Fracture toughness (MPa·m ^{1/2})
C _f /SiBCN	371±31	32±2	188±14	12.9±1.5

Fig. 9 (a) Typical bending stress vs. strain curve and (b)–(d) typical microstructure of fracture surfaces of the $C_f/SiBCN$ composites.

which displays a typical non-brittle failure behavior. The composites extend elastically at the beginning of the bending test until the elastic limit. After that, micro-crack and interfacial debonding take place and pseudo-plastic deformation begins. The stress nonlinearly increases with a further increase of strain until the maximum stress is reached. The load drops abruptly as the first layer of fibers fails. As strain further increases, the second bluff appears, corresponding to the failure of the second layer of fibers in the composites.

Fracture behavior of fiber reinforced composites is primarily dependent on the properties of fiber, matrix, and their interface. Particularly, an appropriate fiber–matrix bonding strength allows for energy consumption via controlled interface debonding and fiber pull-out. Therefore, fiber–matrix interfaces with appropriate bonding strength are important for property optimization of the composites. Figures 9(b)–9(d) show the microstructure of fracture surfaces of the $C_f/SiBCN$ composites. It illustrates an extensive interface debonding and fiber pull-out, which is responsible for the high fracture toughness ($12.9 \text{ MPa}\cdot\text{m}^{1/2}$). The interfacial bonding strength could be roughly evaluated from the morphologies of the fracture surfaces. As shown in Fig. 9(b), a large number of long pulled-out fibers could be seen on the fracture surface. Moreover, the interface with sidestep shape (Fig. 9(b)) indicates that the SiBCN matrix is strongly combined with the interface, resulting

in deflected and elongated crack propagation path. Typical crack propagation, crack arrest, interface debonding, and short fiber pull-out in the $C_f/SiBCN$ composites are shown in Fig. 9(d). Consequently, the $C_f/SiBCN$ composite can consume more energy during fracture, leading to the high fracture toughness [42].

4 Conclusions

In this work, carbon fiber reinforced SiBCN matrix composites ($C_f/SiBCN$) were fabricated by a modified polymer infiltration and pyrolysis (PIP) process, using liquid poly(methylvinyl)borosilazanes (PMVBSZ) as precursor. With dicumyl peroxide (DCP) added as cross-linking agent, the PMVBSZ could be solidified at $120^\circ\text{C}/2 \text{ h}$, which results in a high ceramic yield of $\sim 70\%$ after pyrolysis at $1100^\circ\text{C}/2 \text{ h}$. The cross-linking mechanism, ceramization processes, and microstructure of the obtained SiBCN ceramics were investigated in detail. To improve the infiltration efficiency and protect the precursor against moist air during PIP, a modified infiltration technology was developed for the impregnation process. Consequently, $C_f/SiBCN$ composites with a density of 1.734 g/cm^3 and an open porosity of 10.3% were achieved after only 7 PIP cycles. The flexural strength, tensile strength, and fracture toughness of the fabricated $C_f/SiBCN$ composites are 371 MPa, 188 MPa,

and $12.9 \text{ MPa} \cdot \text{m}^{1/2}$, respectively.

Acknowledgements

The financial supports from the National Key Research and Development Program of China (No. 2017YFB0703200), National Natural Science Foundation of China (No. 51702341), Chinese Academy of Sciences Innovative Funding (No. CXJJ-17-M169), and CAS Pioneer Hundred Talents Program are greatly acknowledged.

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