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Synthesis and ceramic conversion of a novel processible polyboronsilazane precursor to SiBCN ceramic

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Abstract

Polyboronsilazane (PBSZ) precursors for SiBCN ceramics were prepared by using 9-borabicyclo-[1,3,3] nonane (9-BBN) and copolysilazanes (CPSZ) as starting materials, involving the hydroboration reaction between vinyl groups of PSZ and B–H groups of 9-BBN under mild conditions. The as-synthesized PBSZ was obtained as a soluble liquid, which was characterized by FT IR and NMR. The polymer-to-ceramic conversion of PBSZ at a ceramic yield of 62.2–79.9% was investigated by means of FT IR and TGA. The crystallization behavior and microstructures of PBSZ-derived SiBCN ceramics were studied by XRD, SEM and HRTEM. The SiBCN ceramic began to crystallize at 1600 °C. Further heating at 1800 °C induced partial crystallization to give mixed XRD patterns for SiC, Si_3N_4, and BN(C). It is observed that the introduction of boron improves the thermal stability of SiBCN ceramics, especially under high temperatures of 1600–1800 °C. In addition, the introduction of boron significantly improves the ceramic density while inhibits the SiC crystallization.

Keywords: Polyboronsilazane; Silicon carbide; Silicon nitride; Polymer-to-ceramic

1. Introduction

During the past decades, the quaternary silicon–boron–carbon–nitrogen (SiBCN) ceramics with outstanding physical and chemical properties are important materials for fabricating composites, fibers, membranes, and bulk ceramics because of the superior thermal and mechanical properties of multinary systems [1–8]. Because the diffusion coefficients of Si or B in compounds such as nitrides or carbides are extremely low [2], thus the preferable way to prepare SiBCN ceramics is the precursor-derived ceramic method. These results have intensified efforts directed at the design of new processible polyborosilazane (PBSZ) precursors to SiBCN ceramics in technologically useful forms.

Generally, two different approaches to the design of PBSZ have been explored, namely monomer route and polymer route [9]. The monomer route involves the synthesis of polymers from boron-containing monomer units. Hydroboration of vinyl-substituted chlorosilanes and subsequent ammonolysis of resulting hydroborated compounds is a well-established procedure for the preparation of SiBCN polymers [1,10,11]. Riedel et al. [1] reported the ammonolysis of $B[C_2H_4Si(CH_3)Cl_2]_3$ which was prepared via hydroboration between $(CH_3)_2{\cdot}BH_3$ and $CH_3Si(CH{=}CH_2)Cl_2$. After pyrolysis of the resultant PBSZ precursor, the final SiBCN ceramic was stable for a limited time at temperature >2000 °C. They later described the synthesis of polymers having a higher boron content using either $HBCl_2{\cdot}S(CH_3)_2$ or $H_2BCl{\cdot}S(CH_3)_2$ instead of $(CH_3)_2{\cdot}BH_3$ [10]. Similarly, Bernard et al. [11] synthesized a PBSZ by the quantitative hydroboration of the starting dichloromethylvinylsilane with borane dimethylsulfide and the subsequent aminolysis of the resulting monomeric tris(dichloromethylsilylethyl)borane. In addition, hydroboration of unsaturated chlorosilanes as well as hydrosilylation of unsaturated borazines without subsequent ammonolysis was also used to prepare the PBSZ polymers [12–17]. Kim et al. [12–14] prepared a series of PBSZ by a hydroboration reaction between borazine and vinylsilane, trivinylcyclotrisilazane, and tetramethyldivinyldisilazane, respectively. Schmidt et al. [15] prepared the PBSZ precursors via hydroboration and

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dehydrocoupling of vinly-containing cyclotrisilazanes with a borane adduct $BH_3{\cdot}NMe_3$. Nesper et al. [16,17] synthesized borazine precursors for SiBCN ceramics by using hydrosilylation of B, B′, B″-triethynylborazine with $HSiRCl_2$ (R = Cl, Me, Ph). By monomer route, because these polymers are formed by condensation polymerization, it is difficult to attain the high molecular weights and rheological properties that are desired for some applications.

The polymer route involves chemical modification of silicon-containing polymers or oligomers with boron-containing compounds. In general, borazine and boranes are usually used as boron sources. Sneddon and coworkers [18] succeeded in the modification of hydridopolysilazane (HPZ) with borazine, via either hydrogen or trimethylsilane elimination reactions. Subsequently, they prepared three new series of processible polymeric precursors to SiBCN ceramics by reaction of HPZ with monofunctional boranes [19]. Spectroscopic and chemical studies indicate the boranes are attached to the HPZ backbone via B–N linkages that results from dehydrocoupling reactions. A borane adduct $BH_3{\cdot}SMe_2$ was also used as a boron source to prepare the PBSZ. Muller et al. [20,21] reported the preparation of PBSZ via hydroboration of poly(methylvinylsilazane) or oligovinylsilazane with different amounts of $BH_3{\cdot}SMe_2$. Weinmann and coworkers [22,23] synthesized boron-modified polysilazanes of general type $\{B[C_2H_4Si(R)NH]_3\}n$ (R = H, $(NH)_{0.5}$, CH_3) via the hydroboration of polyvinylsilazane with $BH_3{\cdot}SMe_2$. In comparison with the monomer route, an important advantage of this polymer route is the ability to start with a polysilazane with relatively high molecular weights and tailored processing properties.

However, most of the reported preceramic polymers for SiBCN ceramics have been extremely pyrophoric and are insoluble in most solvents, which make them difficult to handle and limits their ability to be processed [13,15,22,23]. The design of new PBSZ precursors with the desired compositions, as well as excellent processibility, continues to be a formidable challenge. In our previous work, we prepared tailorable copolysilazanes (CPSZs) with variable chemical structure and molecular weights by coammonolysis of dichloromethylsilane, dichloromethylvinylsilane and trichloromethylsilane [24]. In this paper, we report the results of our studies, using the polymer route, of the synthesis and polymer-to-ceramic conversion of a new processible PBSZ, which was prepared by hydroboration of the CPSZ with a new boron source of the monofunctional borane, 9-borabicyclo-[3.3.1] nonane (9-BBN).

2. Experimental process

2.1. General

All manipulations were carried out using standard high vacuum or inert atmosphere techniques as described by Shriver and Drezdzon [25]. The CPSZ with an approximate formula of $[SiH(CH_3)NH]_x[Si(CH{=}CH_2)(CH_3)NH]_y[Si(CH_3)NH_{1.5}]_z$ (x:y:z = 1:2.2:1.2) was synthesized according to our previous work [24]. Toluene and hexane were distilled from a sodium benzophenone mixture before use. 9-BBN was purchased from Sigma Aldrich. Other commercially available reagents were used as received.

2.2. Tests and characterization

FT IR spectra (transmission) were recorded on a Nicolet Avator 360 apparatus (Nicolet, Madison, WI) with KBr plates for liquid samples and KBr disks for solid samples. NMR spectrometer (Bruker, Germany) operating at 300.13 MHz for hydrogen-1, 75.46 MHz for carbon-13 (^{1}H decoupling), and 96.96 MHz for boron-11 (^{1}H decoupling). The specimens used for NMR were dissolved in $CDCl_3$ solution. Tetramethylsilane (TMS) was used as an internal standard for ^{1}H and ^{13}C NMR. The chemical shift of ^{11}B NMR was referenced to $BF_3{\cdot}OEt_2$. Thermal analysis of the cured CPSZ and PBSZ was conducted on a thermal gravimetric analysis (TGA) analyzer (Netzsch STA 429CD, Netzsch, Germany) in argon with a ramping rate of 10 °C/min ranging from room temperature (RT) to 1000 °C. X-ray diffraction (XRD) was carried out by using a PANalytical X'Pert PRO diffractometer (PANalytical, Netherlands) with Cu$K\alpha$ radiation. The specimens were continuously scanned from 10° to 90° (2θ) at a speed of 0.0167°/s. Raman spectra were recorded on a Raman spectrometer (LabRam I, Dilor, France). The morphologies of the ceramics were examined with a scanning electron microscope (SEM) (Model 1530, LEO, Germany). Transmission electron microscopy (TEM) observations and high resolution image were performed using a JEM 2100 (JEOL, Japan) operated at 200 kV.

2.3. Polymer synthesis

A series of PBSZs were prepared by hydroboration of CPSZ and different mass fraction of 9-BBN. In a typical reaction, a 50 mL three-necked flask equipped with a magnetic stirrer, a constant-pressure funnel and an argon inlet. Under argon atmosphere, the three-necked flask was added 2.0 g CPSZ first. A certain amount of 9-BBN dissolved in 10 mL dry toluene was added in the constant-pressure funnel, and then the 9-BBN solution was dropped into the three-necked flask with the argon flowing and stirring. After the addition was complete, the reaction mixture was stirred for 24 h at 30 °C. Finally, the solvent was removed under vacuum yielding a viscous translucent oil.

2.4. Polymer-to-ceramic conversion

Thermal curing of the CPSZ and PBSZ was carried out in an argon atmosphere, placed in a 180 °C oil bath for 24 h, then the liquid transformed slowly into a compact, pale, rubbery solid. For $T_p < 900$ °C (T_p being the highest temperature during pyrolysis), the cured sample was put in a graphite crucible and heated in a glass silica tube under an argon flow. The temperature was progressively raised up to T_p at a rate of 5 °C/min and kept at this value for 2 h. For $T_p > 900$ °C, the sample (prepyrolyzed at 900 °C) was put in a graphite paper, heated rapidly to T_p at a rate of 40 °C/min in inert atmosphere, then kept at T_p for 10 min. The resulting ceramic was furnace-cooled to RT.

3. Results and discussion

3.1. Synthesis and characterization of PBSZ

As mentioned above, various borane derivatives have been used as boron sources in the synthesis of polymeric precursors for the SiBCN ceramics [19–23]. The 9-BBN is a monofunctional borane with very high regioselectivities in the hydroboration reactions [26], which is used as a new boron source to modify the CPSZ in our present study. A series of PBSZs were prepared via the hydroboration of CPSZ and 9-BBN. According to the weight ratios of boron element to CPSZ are 1%, 3% and 5%, the as-synthesized products are abbreviated as PBSZ1, PBSZ2 and PBSZ3, correspondingly. The as-synthesized PBSZ is a transparent viscous liquid and is soluble in common organic solvents, indicating its excellent processiblity.

The PBSZs were characterized by means of FT IR and NMR. The functional groups of CPSZ were identified by FT IR (Fig. 1), which was assigned in our previous work [24]. From a comparison of the FT IR spectra of PBSZs with those of CPSZ and 9-BBN, it is observed that PBSZs contain characteristic peaks of CPSZ and 9-BBN. The C–H stretch peak (3055 cm^{-1}) from $CH{=}CH_2$ groups significantly decreased after the hydroboration. On the contrary, the C–H stretch peak (2830–2920 cm^{-1}) due to the 9-BBN increased after the hydroboration. The results suggest the difference in its structure between the CPSZ and PBSZ. Meanwhile, the PBSZ was partially boron-modified because of the presence of residual C=C groups.

According to our previous work [24], the reaction degree of C=C groups ($P_{C=C}$) was determined by FT IR and the results are given in Table 1. Herein, the intensity ratio of the peaks at 3055 cm^{-1} (C=C) to that at 1250 cm^{-1} ($Si–CH_3$) is denoted as $A(C{=}C)/A(Si–CH_3)$ which indicates the C=C content. It shows that with the increase of boron in feed, $A(C{=}C)/A(Si–CH_3)$ value and the $P_{C=C}$ gradually decrease, indicating that C=C bonds are involved in the hydroboration reaction as expected.

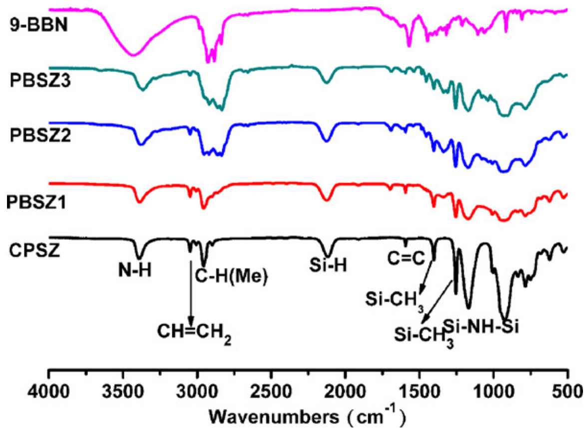
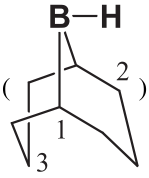


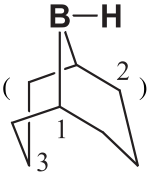
Fig. 1. FT IR spectra of PBSZs, CPSZ and 9-BBN.

Table 1
Synthesis of PBSZs with different amounts of boron.

Polymeric precursor	Boron (wt%)[a]	$A(C{=}C)/A(Si–CH_3)$	$P_{C=C}$ (%)
CPSZ	0	0.18	0
PBSZ1	1	0.165	8.3
PBSZ2	3	0.152	15.5
PBSZ3	5	0.135	25.0

[a] Weight ratios of boron element to CPSZ.

The PBSZs are further characterized by NMR spectra in order to study the influence of B-content on the structure of precursors. The peaks in the ^1H NMR spectra (Fig. 2(a)) consist of complex multiplets and broadened peaks. The peaks at about 1.6 ppm are assigned to the proton absorption peaks of ^1H located position 2 and 3 in 9-BBN () [26,27]. The signal of proton absorption due to $Si–\mathbf{CH_2}^\bullet–\mathbf{CH_2}^\bullet–B$ is buried under multiplet at 0–0.8 ppm. The Si–H bond barely changes before and after the reaction, the characteristic peak remains the same and no other buried peaks at 4.3–5.0 ppm.

As shown in Fig. 2(b), in the $^{13}C\{^1H\}$ NMR spectrum of 9-BBN (), the peaks at about 24 ppm are assigned to the absorption peaks of ^{13}C located position 1, while peaks at about 34 ppm are assigned to ^{13}C located position 2 and 3 [27]. Moreover, the complex multiplets from −3 to 10 ppm are attributed to $Si–CH_3$. It is worth mentioning that the signals at 11 and 16 ppm are due to carbon absorption of newly formed $Si–\mathbf{C}^\bullet H_2–CH_2–B$ and $Si–CH_2–\mathbf{C}^\bullet H_2–B$ units, respectively [10]. The absorption of carbon in $Si–CH_2–CH_2–B$ units enhanced with the increase of 9-BBN in the feed, indicating that hydroboration between 9-BBN and CPSZ did occur. While there are still quite a few of Si–H bonds and double bonds after hydroboration, which would contribute to the followed curing of PBSZ precursor.

The $^{11}B\{^1H\}$ NMR spectrum (Fig. 2(c)) shows a number of peaks, as to 9-BBN, the peak at around 28 ppm is due to the 9-BBN [26,27]. While in the assignments of PBSZ, the multiplets from −4 to 0 ppm are attributed to the boron of $R_3B{:}N$ units, which are formed via the electron-defect boron partially coordinated with lone-pair electron N. The signals at 90 ppm are assigned to the boron that connect with three carbon atoms but not coordinated with nitrogen atom [10,27,28]. Based on the FT IR and NMR results, the reaction between 9-BBN and CPSZ is shown in Scheme 1.

In summary, the reaction between CPSZ and 9-BBN could be divided into two steps. Namely, the first step is hydroboration to form precursor with BC_3 structure in side

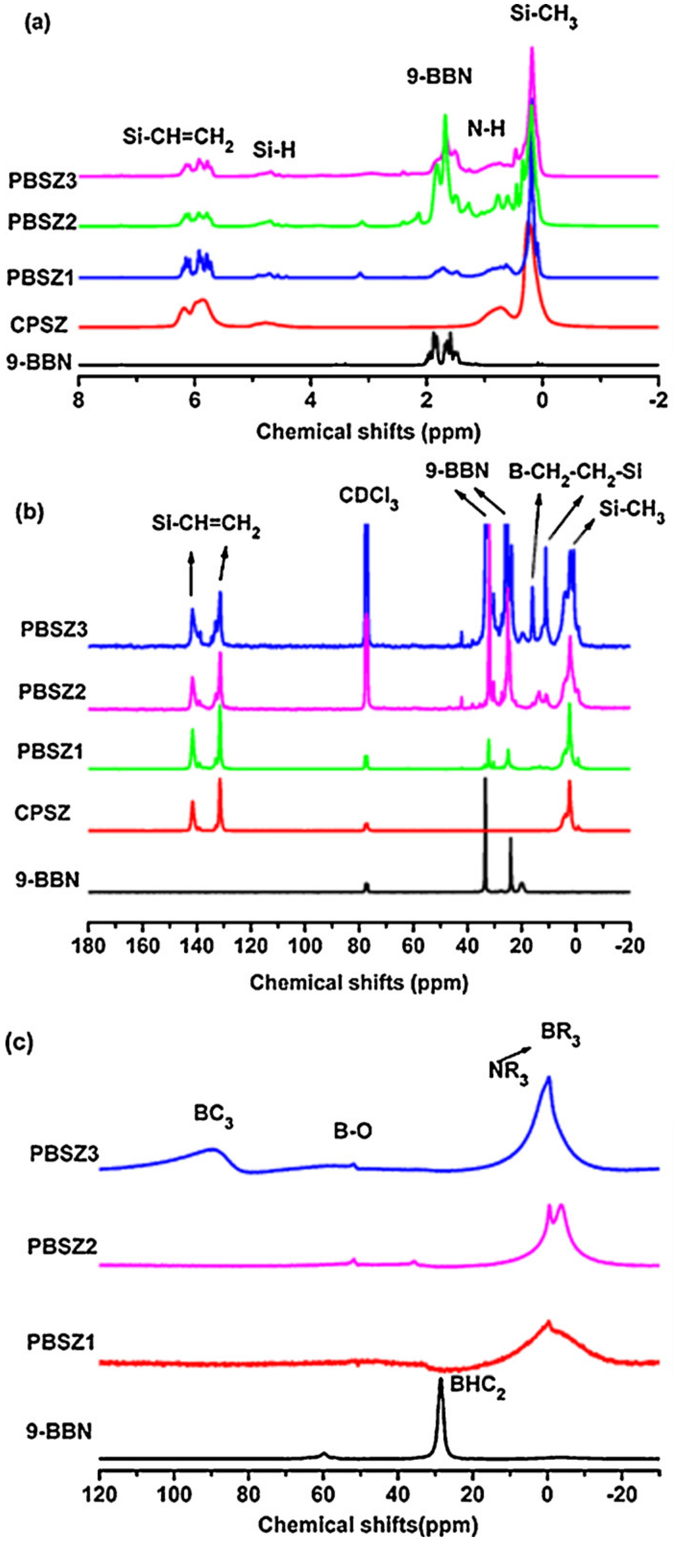


Fig. 2. NMR spectra ($CDCl_3$) of PBSZs with different B-contents: (a) ^1H NMR, (b) $^{13}C\{^1H\}$ NMR and (c) $^{11}B\{^1H\}$ NMR.

chains. In the second step, the boron with strong affinity binds nitrogen to form R_3B:N units, because of the steric hindrance effect of 9-BBN, the N coordinated to B usually comes from another polymer chain.

3.2. Polymer-to-ceramic conversion of PBSZ

For the PBSZs, the element boron connects with the backbone through the chemical bonding, therefore the boron could uniformly distribute in the precursor. In addition, PBSZs have abundant active groups such as C═C, N–H, B–H and Si–H groups, which would improve the cross-linking reaction during the polymer-to-ceramic conversion of the PBSZ precursors.

The FT IR was used to investigate the structural evolution of typical PBSZ3 heat-treated at different temperatures and the results are shown in Fig. 3. From 180 °C to 500 °C, the peaks of N–H (3385 cm^{-1}, 1175 cm^{-1}) and Si–H (2120 cm^{-1}) sharply reduced [24], it mainly happened dehydrogenation coupling and transamination. It is worth mentioning that the intensity of peak at 2830–2920 cm^{-1} due to C–H absorption of 9-BBN gradually reduced and almost vanished at 500 °C, indicating that the decomposition of 9-BBN is completed at 500 °C. From 500 °C to 700 °C, the peaks attributed to N–H and Si–CH_3 (2980 cm^{-1}, 1250 cm^{-1}) further reduced, this is because of the decomposition of organic side groups. Only one broad peak retained when heated to 900 °C, other peaks from organic groups almost disappeared. It is believed that the conversion from polymer to ceramic is complete at 900 °C. When temperature is higher than 900 °C, the spectra of samples heated at different temperatures are similar. At 900 °C, the broad peak from 750 to 1400 cm^{-1} is attributed to B–N (1380 cm^{-1}) [23,28,29], Si–N (1000 cm^{-1}) and Si–C (780, 900 cm^{-1}) [27,28]. With the temperature increasing, the intensity of peak of Si–N weakened, accompanied by the blue shift of B–N peak and sharpening of Si–C peak. The results indicate the formation of crystalline SiC and BN.

To investigate the thermal behavior of the PBSZ accompanied by its structural evolution, TGA curves of PBSZs are shown in Fig. 4. According to our previous work, three main regions can be identified in the weight loss curves of the CPSZ. The weight losses are 0.9% (180–300 °C), 4.1% (300–500 °C) and 14.8% (500–900 °C). For the PBSZ systems, the corresponding weight losses are 2.6% for PBSZ1, 12.5% for PBSZ2, and 13.7% for PBSZ3 in the region of 100–300 °C. In the region of 300–500 °C, the weight losses are 7.0% for PBSZ1, 23.2% for PBSZ2, 28.0% for PBSZ3. In the region of 500–900 °C, the weight losses are 13.1% for PBSZ1, 12.9% for

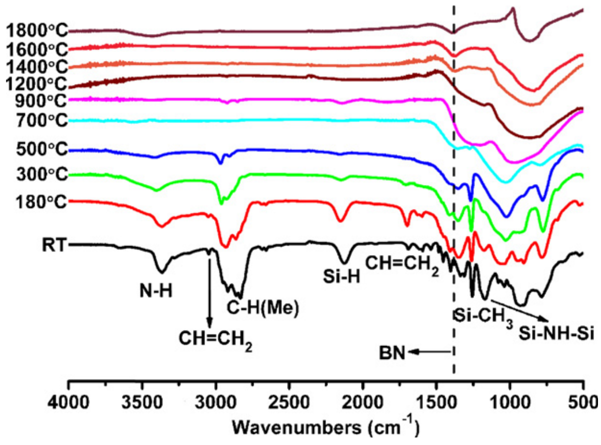
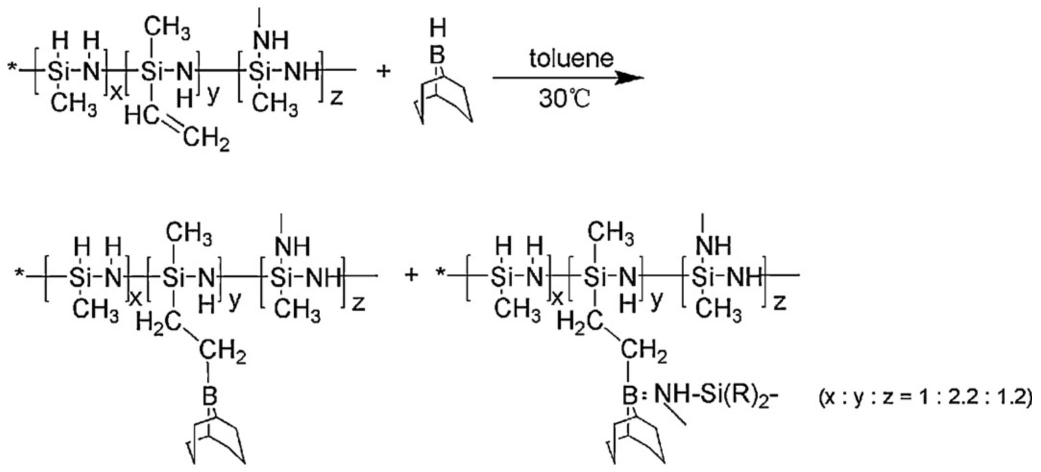


Fig. 3. FT IR spectra of PBSZ3 heat-treated at different temperatures.



Scheme 1. Hydroboration reaction of CPSZ with 9-BBN.

PBSZ2, 9.6% for PBSZ3. Below 500 °C, the weight loss of PBSZ is much higher than that of CPSZ, which might be due to the evaporation of unreacted 9-BBN and the decomposition of naphthenic base in reacted 9-BBN. The more the addition of 9-BBN, the more the weight loss. According to the FT IR results, the decomposition of reacted 9-BBN is completed at 500 °C, which supports the changes of PBSZ TGA curves below 500 °C. On the contrary, the weight loss of PBSZ is lower than that of CPSZ in the region of 500–900 °C. During this temperature range, dehydrogenation and demethanation reactions are involved, and the evolution of H_2 and CH_4 gases is responsible for the weight loss. Based on the TGA results, it seems that the boron might react with the CH_4 to generate boron carbide, which inhibits the weight loss of polymeric precursors in the region of 500–900 °C. The more the addition of 9-BBN, the less the weight loss. Generally speaking, the 1000 °C ceramic yields of PBSZs ranges from 62.2% to 79.9%.

3.3. Ceramic crystallization

To investigate the crystallization behavior of pyrolyzed PBSZ, XRD patterns of the samples were measured. In Fig. 5, at 900 °C, the ceramic is amorphous and highly disordered. Further heating at 1200 °C, the peak of graphite appears. At 1600 °C, a broad peak appears at about 36°, indicating the incomplete crystallization and the formation of β-SiC. The characteristic peaks of β-SiC appear until 1800 °C, the three major peaks at $2\theta = 36°$ (1 1 1), 60° (2 2 0), 72° (3 1 1), along with the peak at $2\theta = 34°$ are attributed to α-SiC [30]. In addition, the weak peaks of β-Si_3N_4 appear at $2\theta = 23°$ (1 1 0), 27° (2 0 0), 52° (3 0 1) and 70° (3 2 1) [16,20,23]. The h-BN phase with the (0 0 2) ($2\theta = 26.7°$) and (1 0 0) ($2\theta = 41.6°$) diffraction planes is observed [11,31]. However, there is no evidence for the formation of crystalline h-BN since the graphite diffraction planes overlap with the (0 0 2) ($2\theta = 26.7°$) planes. Because of their disordered two-dimensional (turbostratic) structure, BN layers are always not detected by XRD [1,7,22,23].

The influence of boron contents on the crystallization behavior of SiBCN ceramics was also investigated. It can be seen in Fig. 6(a) that the characteristic peaks of β-SiC and α-SiC appear in the CPSZ derived ceramic at 1600 °C. While there are only broad peaks of α-Si_3N_4 and β-SiC in the PBSZ derived ceramic at 1600 °C. Moreover, Fig. 6(b) shows that CPSZ, PBSZ1 and PBSZ2 pyrolyzed at 1800 °C only have the

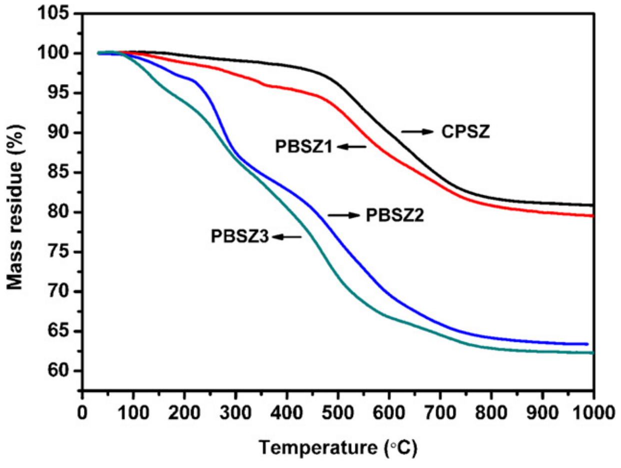


Fig. 4. Thermal gravimetric analysis (TGA) curves of the cured PBSZs at a heating rate of 10 °C/min under argon.

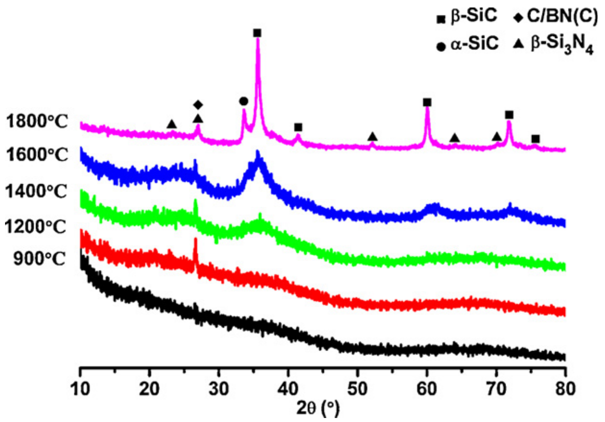


Fig. 5. X-ray diffraction patterns of PBSZ3-derived ceramics pyrolyzed at different temperatures.

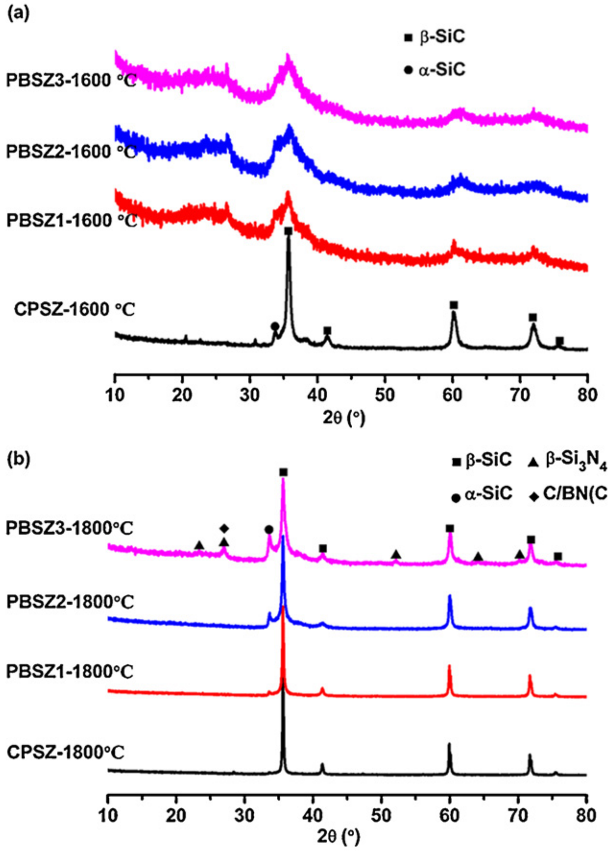


Fig. 6. X-ray diffraction patterns of samples with different B-contents: (a) heat-treated at 1600 °C and (b) heat-treated at 1800 °C.

crystal peak of SiC while the peak of Si_3N_4 disappears. When the B-content in the feed is 5%, there is still a little crystal of β-Si_3N_4, indicating that the boron restrains the decomposition of Si_3N_4. In addition, the apparent grain-size of β-SiC at 1800 °C was calculated by Scherrer equation. The apparent grain-size of β-SiC of CPSZ-derived ceramic is 97 nm, while those of CPSZ1, CPSZ2, and CPSZ3-derived ceramics are 63 nm, 27 nm, and 16 nm, respectively. With the increase in boron content of polymeric precursors, the grain size of β-SiC gradually reduced, demonstrating that boron can effectively inhibit the grain growth and improve the resistance to high temperature. Meanwhile, it is worth mentioning that the boron inhibits the decomposition of Si_3N_4.

In order to investigate the thermal stability of the final SiBCN ceramics, the weight residue of 900 °C ceramics after heated-treated at different temperatures is shown in Fig. 7. Generally, the weight residue of SiBCN is significantly higher in comparison with that of the CPSZ-derived SiCN ceramic. The higher the boron content in the feed is, the higher the weight residue is. Especially in the range of 1400–1600 °C, the weight loss of CPSZ, PBSZ1, PBSZ2, and PBSZ3-derived ceramics is 31.6%, 11.3%, 7.3% and 5.6%, respectively. The results suggest that the weight loss is significantly inhibited by the introduction of boron into the ceramics. As is well-known for the SiCN ceramics, a decomposition reaction occurs above 1400 °C [1,20–22], which involves excess carbon reacting with Si_3N_4 shown in Eq. (1).

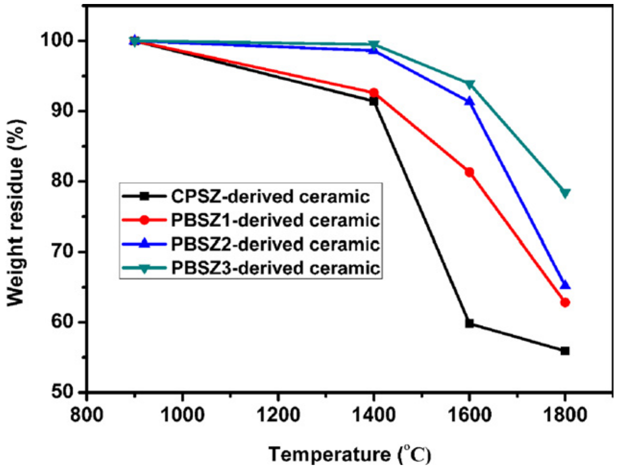


Fig. 7. Weight residues of 900 °C ceramics after heated-treated at different temperatures.

$$Si_3N_4 + 3C(\text{freecarbon}) \rightarrow 3SiC + 2N_2 \qquad (1)$$

We infer that the inhibition of weight loss works through three routes: (1) The BN has much better thermostability than Si_3N_4. (2) The BN could combine free carbon to form BN(C), which has low activity and impede the decomposition reaction of Si_3N_4 [22]. (3) The BN(C) layer disperses in the crystal boundary and blocks the interdiffusion of different parts of composition, leading to the local pressure of N_2 increasing [28]. As a result, the decomposition temperature would be raised. Namely, the N_2 evolution derived from the decomposition decreases, which inhibits the weight loss of heated-treated ceramics in the range of 1400–1600 °C. For the higher boron content containing system, even Si_3N_4 crystallization remained at 1800 °C, shown in Fig. 6(b). In summary, it confirms the advantage influence of boron on the stability of SiBCN ceramics under high temperatures.

3.4. Ceramic microstructure

In order to study the effect of introduction of boron on the microstructure of ceramics, the samples pyrolyzed at different temperatures were analyzed using SEM. The SEM fracture surface imagings of the specimens heated at 1600 °C and 1800 °C are shown in Fig. 8. There are lots of micropores in the CPSZ heat-treated at 1600 °C, while the ceramics derived from the PBSZ1 and PBSZ3 are more compacted with few pores. Moreover, the crystallite dimension decreases with the addition of boron. The specimens heat-treated at 1800 °C are also observed by SEM. Similar to the trend at 1600 °C, the ceramics' density increases while the crystallite dimension decreases with the introduction of boron into the ceramics. It can be deduced that the addition of a small amount of boron could improve the density of ceramics and inhibit the SiC and Si_3N_4 crystallization.

TEM images in Fig. 9 demonstrate that the final ceramic annealed at 1800 °C consists of SiC, Si_3N_4 and BN(C)

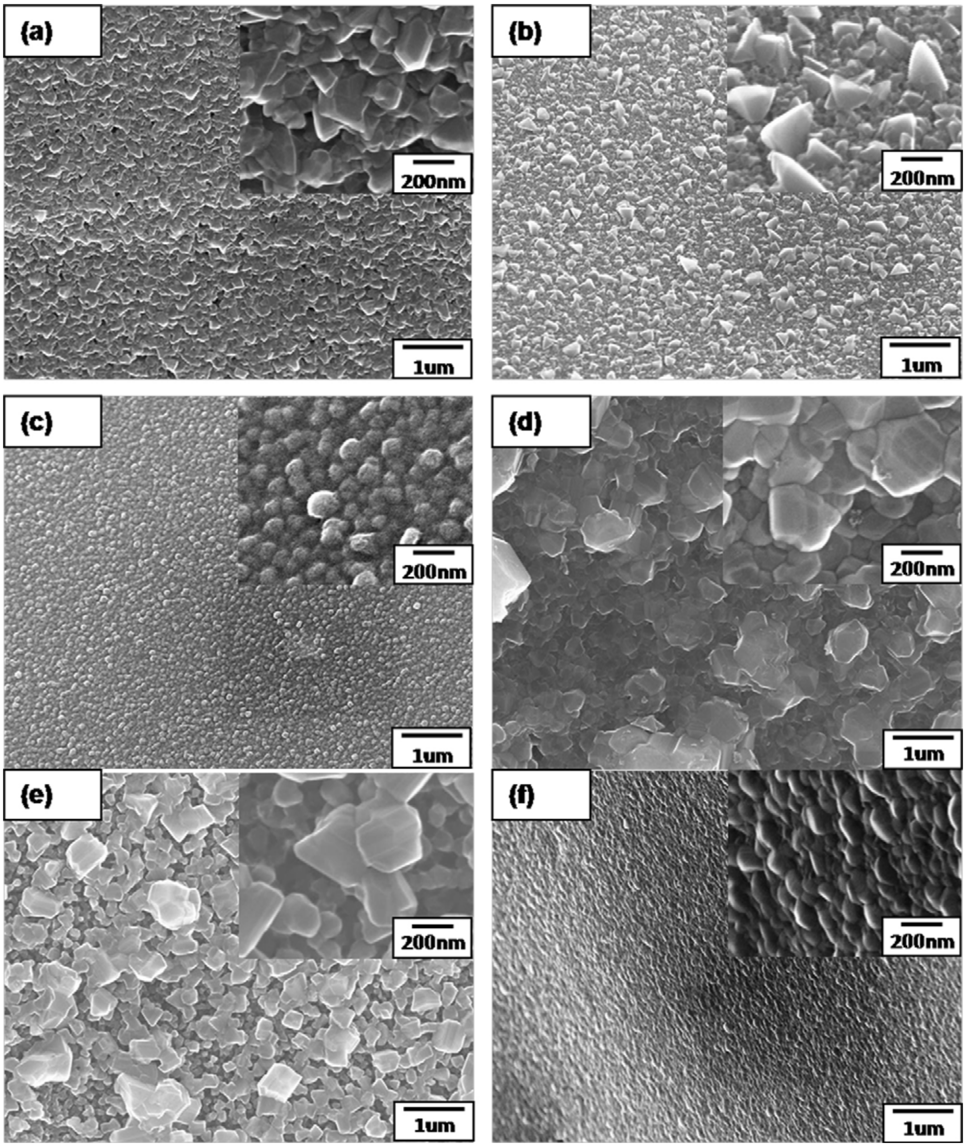


Fig. 8. HRSEM images of samples pyrolyzed at 1600 °C: (a) CPSZ, (b) PBSZ1, (c) PBSZ3 and at 1800 °C: (d) CPSZ, (e) PBSZ1, (f) PBSZ3.

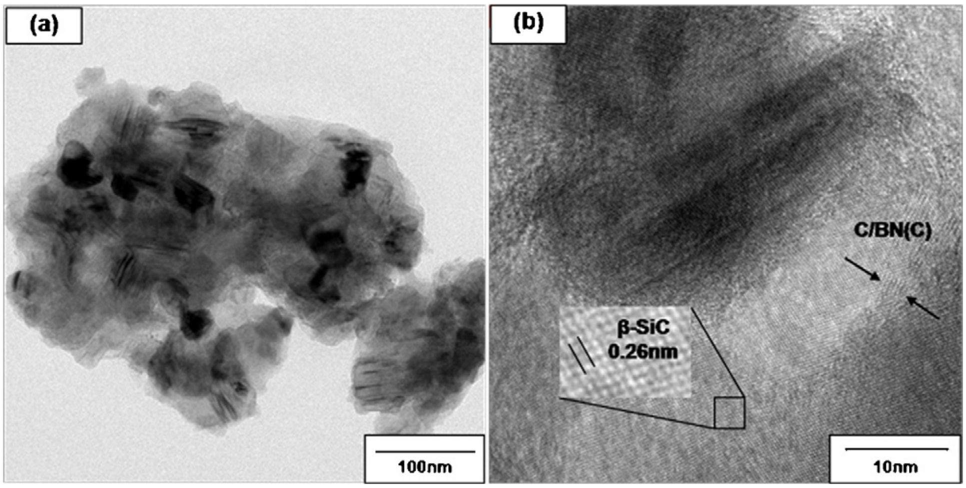


Fig. 9. Bright field image (a) and HRTEM image (b) of PBSZ-3-derived ceramic pyrolyzed at 1800 °C.

nanocrystallites with grain sizes in the range 20–30 nm, which is consistent with the XRD results. Turbostratic BN(C) interface layers exist, which are considered as diffusion barriers at higher temperatures, thus inhibiting decomposition reactions [22].

4. Conclusions

In this paper, a processible PBSZ was successfully prepared by hydroboration of CPSZ and 9-BBN. The as-synthesized PBSZ was characterized by FT IR and NMR. It is confirmed that CPSZ firstly reacted with 9-BBN to form polymer precursor with a BC_3 side chain, subsequently, the electron-defect boron partially coordinated with lone-pair electron N to form the R_3B:N units.

The polymer-to-ceramic conversion of the PBSZ was investigated by means of FT IR and TGA. The 1000 °C ceramic yields of PBSZs ranges from 62.2% to 79.9%, which relies on the 9-BBN contents in the feeds. The crystallization behavior and microstructure of PBSZ-derived SiBCN ceramics were studied by XRD, SEM and HRTEM. The SiBCN began to crystallize at 1600 °C, and partially crystallized at 1800 °C to show mixed XRD patterns for SiC, Si_3N_4, and BN(C). It is observed that the introduction of boron improves the thermal stability of SiBCN ceramics, especially under high temperatures of 1600–1800 °C. In addition, the introduction of boron significantly improves the ceramic density while inhibits the SiC crystallization. The liquid characteristic makes the PBSZ excellent potential candidates for a matrix source for fiber-reinforced ceramic matrix composites and for high-temperature protective coating applications.

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