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Ceramics International 38 (2012) 6321–6326
CERAMICS INTERNATIONAL
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A novel polyborosilazane for high-temperature amorphous Si–B–N–C ceramic fibres

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Received 3 March 2012; received in revised form 30 April 2012; accepted 1 May 2012
Available online 14 May 2012

Abstract

Polyborosilazane synthesised from BCl_3, $HMeSiCl_2$, and $Me_3SiNHSiMe_3$ is easy to cross-link for dehydrogenation of Si–H and N–H, which limits its practical applications for Si–B–N–C fibres on an industrial scale. Therefore, in this context, $MeSiCl_3$ was used instead of $HMeSiCl_2$ to synthesise a novel polyborosilazane with limited cross-linking density to fabricate Si–B–N–C fibres. The polyborosilazane synthesised from BCl_3, $MeSiCl_3$, and $Me_3SiNHSiMe_3$ exhibits good melt-processability and 1 km long polyborosilazane fibre can be obtained by melt spinning. Prior to pyrolysis, chemical curing with vapour $HSiCl_3$ at 80 °C was utilised to make the λ green fibres infusible. The as-cured fibres were subsequently pyrolyzed at 1200 °C in nitrogen atmospheres to provide Si–B–N–C ceramic fibres with ca. 1.5 GPa in tensile strength, ca. 160 GPa in Young's modulus, ca. 12 μm in diameter and keeping amorphous up to 1700 °C, which makes them to be promising reinforcements in ceramic matrix composites for high temperature applications.

Keywords: B. Fibres; C. Thermal properties; Polyborosilazane; Si–B–N–C fibres

1. Introduction

Due to its specific properties, i.e., high temperature thermal stability, high mechanical strength, high-temperature creep resistivity, low density, and stability against oxidation or molten silicon, Si–B–N–C ceramic fibre is a suitable candidate as reinforcement in ceramic matrix composites for high temperature applications [1–6]. The polymer-derived ceramics (PDCs) route is the only effective approach known for the preparation of Si–B–N–C fibres. Recently, the Si–B–N–C fibres keeping amorphous up to 1700 °C were successfully prepared from single source precursors such as $B(C_2H_4SiCH_3Cl_2)_3$ [5,6], $Cl_3Si–NH–BCl_2$ [1–3] or $MeCl_2Si–NH–BCl_2$ [7,8], and polyborosilazane [9–11] synthesised from boron trichloride (BCl_3), dichloromethylsilane ($HMeSiCl_2$), and hexamethyldisilazane (HMDS) through PDCs in our lab and elsewhere. Single source precursor routes are multiple-step processes, and byproducts need to be removed separately [3,5,8]. The synthesis process of polyborosilazane (PBSZ-1) from BCl_3, $HMeSiCl_2$, and HMDS via one-pot routes proves to be simpler and cheaper, and byproducts can be removed directly [9]. However, the cross-linking reaction of PBSZ-1 is difficult to control at the end of the synthesis process because of the dehydrogenation of Si–H and N–H of the polymer, which hampers its practical applications on an industrial scale [12].

One way to control the cross-linking reaction is to remove the Si–H groups or N–H groups in the starting monomers. To achieve this objective, in this study, trichloromethylsilane ($MeSiCl_3$) was used instead of $HMeSiCl_2$ to synthesise a novel polyborosilazane with limited cross-linking density to fabricate Si–B–N–C fibres, and the synthesis of the polyborosilazane (PBSZ-2) from BCl_3, $MeSiCl_3$, and HMDS was studied, referring to the synthesis process of PBSZ-1. The PBSZ-2 exhibited good melt-processability and 1 km long PBSZ-2 fibres could be easily obtained by melt spinning. The PBSZ-2 fibres could be cured by $HSiCl_3$ at 80 °C. As-cured fibres were then pyrolyzed in a nitrogen atmosphere

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http://dx.doi.org/10.1016/j.ceramint.2012.05.001

at 1200 °C yielding high temperature amorphous Si–B–N–C fibres up to 1700 °C.

2. Experimental

2.1. General comments

All reactions were carried out in a dry nitrogen atmosphere using Schlenk-type techniques as described by Shriver [13]. BCl_3 (Guangming Special Gas Corp., China) was maintained in n-hexane in refrigerator. $MeSiCl_3$ (Xinghuo Chemical Corp., China) and HMDS (Guibao Chemical Corp., China) were distillated before use.

The chemical compositions of PBSZ-2 were obtained by elemental analysis performed using various apparatus. The silicon and boron elements were quantified by means of ICP-AES using an Arl 3580B spectrometer. Nitrogen and oxygen elements were measured by a Leco TC-436 O/N analyser, and carbon element was measured by a Leco CS-444 C/S analyser.

The chemical structure of PBSZ-2 was determined by Fourier transform infrared (FT-IR) spectroscopy using a Nicolet Avatar 360 apparatus in a KBr pellet. ^{11}B- and ^{29}Si-nuclear magnetic resonance (NMR) spectra were obtained using a Bruker Advance 400 MHz apparatus in $CDCl_3$. Tetramethylsilane (TMS) and $BF_3 \cdot OEt_2$ were used as internal standards for ^{29}Si –NMR and ^{11}B –NMR.

Rheological measurements were carried out in a nitrogen atmosphere by means of an AR200EX oscillatory rheometer. Dynamic measurements were carried out in the linear viscoelastic region obtained by strain sweep tests (see Fig. S1 in Supporting Information), using controlled strain amplitude. Fig. S1 displays a constant high plateau value with a critical strain γ_c of about 15%, from which rheological parameters are modified. It is therefore reasonable to propose that $\gamma_0 = 10\%$ represents an appropriate value to maintain constant dynamic moduli with deformation amplitude. So, the dynamic rheological plot presented in this work corresponds to that selected γ_0. Thermogravimetric analyses (TGA) were conducted using a NETZSCH STA 449C instrument under Ar atmospheres with a heating rate of 5 °C/min.

The microstructures of PBSZ-2 and Si–B–N–C fibres were observed by a S4800 scanning electron microscopy (Hitachi, Japan). Single filament tensile properties were determined using an YG-type tensile strength tester (Jiangsu Taicang Textile Instruments Co., China) with a gauge length of 25 mm. 25 single filaments were tested. The crystallisation of amorphous Si–B–N–C fibres was investigated in graphite furnaces in Ar atmospheres from 1400 to 1800 °C with a heating rate of 10 °C min^{-1} (holding for 1 h each). X-ray diffraction (XRD) was performed on ground-up fibres using a D8 ADVANCE instrument (Cu-Kα radiation).

2.2. Synthesis of PBSZ-2

Typically, the molar ratio of BCl_3, $MeSiCl_3$ and HMDS was 1:1:6. BCl_3 in 1.5 M-hexane solution and $MeSiCl_3$ were introduced into a pre-cooled reactor with a syringe. HMDS was introduced into a dropping funnel and then added dropwisely to the pre-cooled reactor under vigorous stirring. A homogeneous solution without precipitation was obtained by dropwise addition. The temperature of the mixture was kept below 0 °C until the addition completed. Then, the reaction mixture was heated to 140 °C, resulting in volatilization of $SiMe_3Cl$ (b.p. 58 °C) and hexane (b.p. 69 °C). Continued heating up to the maximum reaction temperature of 300–350 °C resulted in volatilization of a mixture of $SiMe_3Cl$ and HMDS (b.p. 126 °C). At the end of the synthesis process, the reaction mixture was held at the maximum temperature for 10–20 h. The final traces of starting reagents, solvent, byproducts and low molecular oligomers were removed at 240–300 °C under a vacuum for 1 h. After cooling to ambient temperature, a yellow transparent bulky solid sensitive to moisture was obtained. The yield of product was greater than 90% of theory, based on the weight of boron in BCl_3. The bulk product was transferred and stored in a glove box.

2.3. Preparation of Si–B–N–C fibres

PBSZ-2 green fibres were prepared using a lab-scale melt-spinning system which was set up inside a nitrogen-filled glove box. The PBSZ-2 was first fed into an extruder, then heated, sheared, and pressured through a filtering system to eliminate any gels or unmelts. Then, the molten PBSZ-2 passed through a single-capillary spinneret of 0.25 mm in diameter. The extrudate flowing PBSZ-2 was then uniaxially drawn to filament, which was subsequently stretched and collected on a rotating spool.

The curing and pyrolysis of the PBSZ-2 fibres were performed in the same high temperature silicate tube furnace. After adding the PBSZ-2 fibres, the furnace tube was purged by a vacuum and subsequently filled with ultra-high pure nitrogen atmospheres three times repeatedly at room temperature to remove the air. Then, the PBSZ-2 fibres were cured by passage of vapour $HSiCl_3$ with a flowing nitrogen atmosphere (50 mL/min) in the tube furnace, and the tube furnace was heated to 80 °C for 1 h (heating rate 4 °C/min). After the curing reaction, a flowing ultra-high pure ammonia atmosphere (25 mL/min) was utilised to react with possible residual Si–Cl bond in $HSiCl_3$ at 80 °C for 0.5 h. Then, the furnace was heated to 1200 °C and held for 1 h (heating rate 5 °C/min) under a flowing purified nitrogen atmosphere (100 mL/min). Cooling the furnace in ambient air to room temperature, black Si–B–N–C ceramic fibres were obtained.

3. Results and discussion

3.1. Synthesis of PBSZ-2

As our previous experiments [9–14], BCl_3 and $MeSiCl_3$ reacted with HMDS by elimination of $SiMe_3Cl$ during the initial stage, and the resulting intermediate molecules self-condensed with the liberation of HMDS at the second stage. But the cross-linking reaction was not found as the reaction mixture never cross-linked during the whole holding time at the maximum reaction temperature ca. 350 °C of PBSZ-1. After vacuum evaporation of low weight oligomers, the obtained PBSZ-2 is a yellow transparent solid that is sensitive to moisture and soluble in common organic solvents, including hexane and chloroform. The elemental analysis results show that the chemical compositions of PBSZ-2 are Si (29.25 wt%), B (6.54 wt%), N (25.26 wt%), C (28.92 wt%), H (9.41 wt%), and O (0.62 wt%). Oxygen content is <1 wt% and could be omitted. Therefore, PBSZ-2 has an empirical formula $Si_{1.7}B_{1.0}N_{3.0}C_{4.0}H_{15.5}$.

The structure of PBSZ-2 is similar to that of PBSZ-1 except that no Si–H or $SiHCN_2$ group was observed in the PBSZ-2, which was identified by FT-IR spectrum (Fig. 1), ^{29}Si –NMR spectrum (Fig. 2), and ^{11}B –NMR spectrum (Fig. 3).

As shown in Fig. 1, the PBSZ-2 and PBSZ-1 have similar characteristic absorption bands: N–H (3430 cm^{-1}), C–H (2958, 2898 cm^{-1}), B–N (1460, 1386 cm^{-1}), Si–CH_3 (1252 cm^{-1}), Si–N (930 cm^{-1}), and Si–$(CH_3)_3$ (839, 769, 683 cm^{-1}) [9,14,15]. But PBSZ-2 has no Si–H (2120 cm^{-1}) (Fig. 1a). The FT-IR spectrum indicates the as-synthesised PBSZ-2 has similar structures to PBSZ-1 except Si–H group.

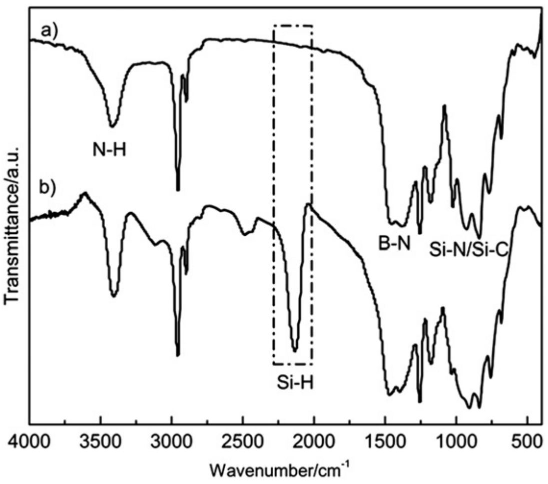


Fig. 1. FT-IR spectra of as-synthesised PBSZ-2 (a) and PBSZ-1 (b).

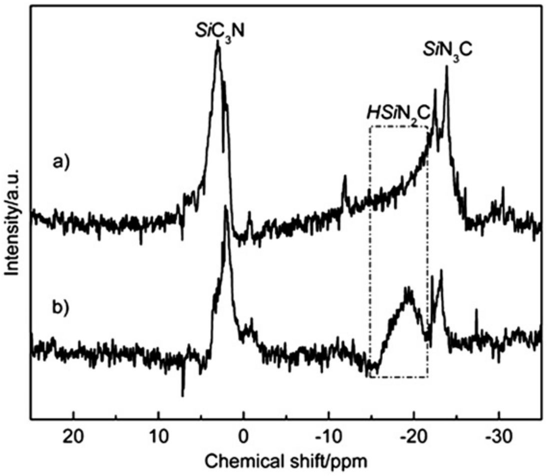


Fig. 2. ^{29}Si –NMR spectra of as-synthesised PBSZ-2 (a) and PBSZ-1 (b).

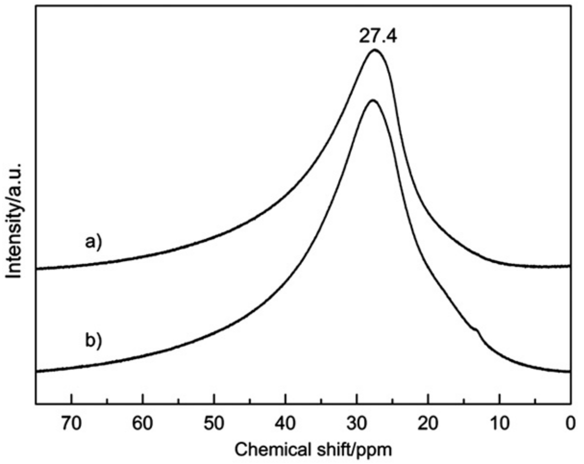
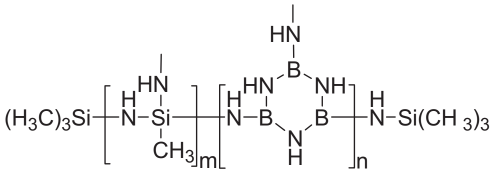


Fig. 3. ^{11}B –NMR spectra of as-synthesised PBSZ-2 (a) and PBSZ-1 (b) in $CDCl_3$.



Scheme 1. Supposed structure of as-synthesised PBSZ-2.

The ^{29}Si –NMR spectra of the solution of PBSZ-1 and PBSZ-2 in $CDCl_3$ (Fig. 2) show similar SiC_3N environment at 2.8∼3.5 ppm and SiN_3C environment at 22∼24 ppm, except that PBSZ-2 has no $SiHCN_2$ environment at ca. 19.8 ppm [9].

Besides, the ^{11}B –NMR spectrum of PBSZ-2 in $CDCl_3$ (Fig. 3a) show a similar single peak centred at 27.4 ppm to that of PBSZ-1 [9], which indicates they have the similar borazinic BN_3 environment.

According to the experiment process and the structure analysis of the PBSZ-2 and PBSZ-1, the structure of PBSZ-2 was supposed as Scheme 1.

3.2. Preparation of PBSZ-2 fibres

A controllable rheology for good processability is a pre-requisite for polymer that would be used as precursor for ceramic fibre. To study the ability of PBSZ-2 for melt-spinning, the oscillatory shear flow of PBSZ-2 was investigated by oscillatory rheometer.

The pre-requisite condition for melt-spinnable polymers is that the polymer should exhibit shear-thinning behaviour, which guarantees that the polymer could be extruded through the spinneret. Secondly, from the point

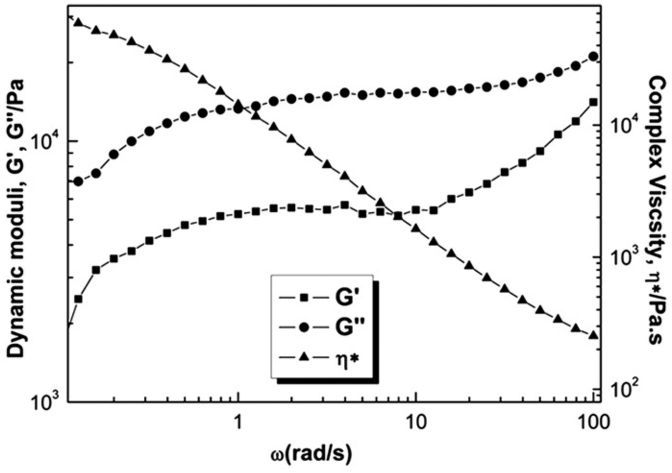


Fig. 4. Frequency dependence of G′, G″, and η* for PBSZ-2 at T_{spin}= 240 °C.

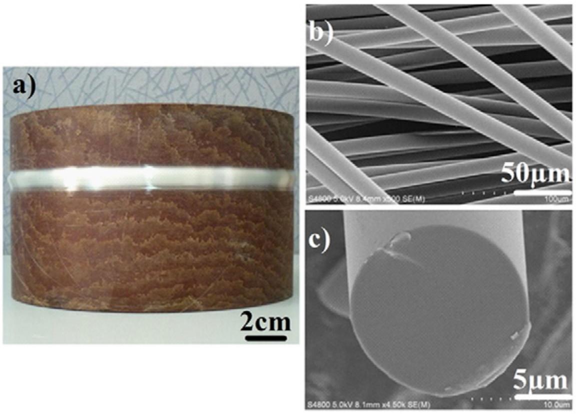


Fig. 5. Morphology of the as-obtained PBSZ-2 fibres. (a) The as-spun PBSZ-2 fibres collected by spool. (b) Surface microstructures of PBSZ-2 fibres. (c) Cross-section microstructure of PBSZ-2 fibres.

of view of oscillatory shear, the loss modulus G″ should be higher than the storage modulus G′ in the spinning frequency range to allow fibre formation during extrusion of the polymer, and a minimum level of G′ is required to allow fibre drawing into a fine-diameter solid filament during winding [16]. As shown in Fig. 4, the complex viscosity $\eta*$ of PBSZ-2 decreases with increasing oscillatory frequency ω, indicating that PBSZ-2 exhibits shear-thinning behaviour. The value of G″ is larger than that of G’ in all the test frequency range, and the G″ and G′ continue to increase in the oscillatory frequency range. Especially, the G′ is in the range $1\times10^3\sim1\times10^4$ Pa in the whole test frequency range. All the viscoelastic properties indicate PBSZ-2 should have good melt-spinnability.

Furthermore, using a lab-scale melt-spinning apparatus, the PBSZ-2 could be easily spun at 240 °C through a capillary of a single-hole spinneret of 0.25 mm in diameter. The resulting colourless and flexible endless filament fell and were immediately taken up on a rotating spool. Without optimising the conditions, PBSZ-2 green fibres were extruded and could be stretched by the spool at a rotation rate of ca. 150 m min^{-1} to produce flexible endless fibres with diameter of ca. 18 μm, which were continuously collected on the spool lasting for at least 30 min (Fig. 5). The spinning temperature of PBSZ-2 (240 °) is higher than that of PBSZ-1 (80～90 °), facilitating the subsequent processes such as the curing of the green fibres, the rotation rate of PBSZ-2 increased from 3.2 cm min^{-1} of PBSZ-1 to 150 m min^{-1}, and spinning stability were raised greatly to 30 min [9], which proved that PBSZ-2 was more suitable to be applied on an industrial scale. Moreover, a pilot plant is building for the production of PBSZ-2 fibres.

3.3. Preparation of Si–B–N–C fibres

As-spun fibres were cured and subsequently pyrolyzed to produce Si–B–N–C ceramic fibres.

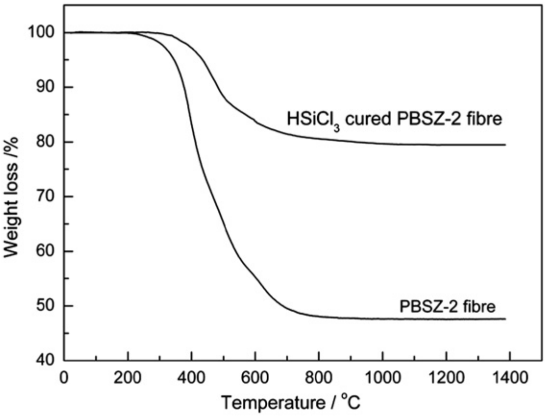
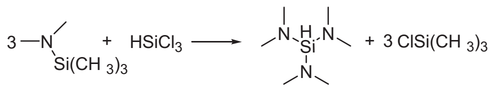


Fig. 6. TG curves of PBSZ-2 fibres and HSiCl$_3$ cured PBSZ-2 fibres from room temperature to 1400 °C under Ar atmospheres.

The weight change of the as-spun green PBSZ-2 fibre was measured by TG upon heating up to 1400 °C in Ar atmospheres. As shown in Fig. 6, the PBSZ-2 fibre shows almost no weight loss up to 300 °C. Most of the weight loss occurs between 300 °C and 800 °C. The PBSZ-2 fibre exhibits a ceramic yield of 47.6 wt% at 1000 °C and even shows almost no weight loss up to 1400 °C. In comparison with our previous works [9], the ceramic yield of PBSZ-2 fibre is lower than that of PBSZ-1 for the lack of potential cross-linking sites (e.g., Si–H) which are pre-requisites for high ceramic yield, but it is expected to increase if the PBSZ-2 fibre is cured prior to pyrolysis.

Owing to the low ceramic yield, the integrity of PBSZ-2 fibres cannot be preserved during heat treatment. It is therefore necessary to investigate an appropriate curing process to render the green fibres infusible by improving the cross-linking density of the polymer and, therefore, its ceramic yield during the polymer-to-ceramic conversion. Generally, polymer fibres with $Si(CH_3)_3$ units can be cured by exposing them into a multifunctional chlorosilane of general formula $RSiCl_3$ at a temperature above the boiling point of the chlorosilane but below the softening



Scheme 2. Supposed curing mechanism of PBSZ-2 fibres .

point of the polymer fibres [17]. In this study, $HSiCl_3$ was used to cure PBSZ-2 fibres. The curing mechanism was supposed as Scheme 2. Firstly, the $HSiCl_3$ could react with $Si(CH_3)_3$ units to cure PBSZ-2 fibres. Secondly, the Si-H units of $HSiCl_3$ could further react with N–H units in the polymer to increase the cross-linking density. Lastly, possible residual Si–Cl bonds could react with flowing NH_3 atmospheres into Si–NH_2 and cross-link during the subsequent pyrolysis process.

The effect of this curing process on the PBSZ-2 fibres was monitored by TG. As shown in Fig. 6, TG profiles indicate that the major difference in weight loss between as-spun PBSZ-2 fibres and the $HSiCl_3$ cured PBSZ-2 fibres occurs in the temperature range between 400 °C and 700 °C, and the ceramic yield of the $HSiCl_3$ cured PBSZ-2 fibres is 80 wt%, much higher than that of the as-spun PBSZ-2 fibres (47.6 wt%). That is because between 400 °C and 700 °C the PBSZ-2 fibres decomposed or rearranged from the polymeric structure to the ceramic phase mainly involving the thermal decomposition of the end group CH_3 [9], and most of the $Si(CH_3)_3$ units in the PBSZ-2 fibres were first removed by $HSiCl_3$ during the curing process. Therefore, exposure of PBSZ-2 fibres to $HSiCl_3$ was an effective way to cure PBSZ-2 fibres.

The $HSiCl_3$ cured PBSZ-2 fibres were pyrolyzed in a flowing nitrogen atmosphere at 1200 °C to yield black Si–B–N–C ceramic fibres. Fig. 7 shows the typical morphology of the as-obtained Si–B–N–C ceramic fibres. The fibres are almost circular which means that the curing and pyrolysis processes retain the fibre shape and no inter-fibre fusion occurs, and exhibit a dense texture with a glassy-like section and uniform surfaces free of apparent defects. Moreover, the Si–B–N–C ceramic fibres with typical diameter of 12 μm exhibit good mechanical properties at room temperature with tensile strengths of 1.5 ± 0.4 GPa and Young's modulus of 160 ± 32 GPa, which reflects the great potential of these Si–B–N–C fibres for reinforcing ceramic matrix composites.

The as-obtained Si–B–N–C fibres were heat-treated at the temperature range 1400–1800 °C for 1 h in an Ar atmosphere, then characterised by XRD. As shown in Fig. 8, there are not any sharp diffraction peaks for the samples heat-treated at below 1700 °C, indicating the amorphous structure of the Si–B–N–C fibres even after annealing at 1700 °C. Nevertheless, heat-treatment at 1800 °C for 1 h leads to segregation of silicon nitride, silicon carbide, and boron nitride crystals. The result shows that the the Si–B–N–C fibres have high-temperature stability up to 1700 °C, which is consistent with those of PBSZ-1 derived Si–B–N–C ceramics of our previous works [9,10].

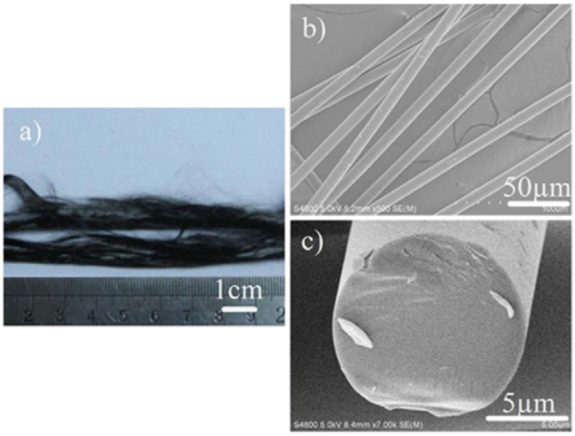


Fig. 7. Morphology of the as-obtained Si–B–N–C ceramic fibres. (a) The as-pyrolyzed Si–B–N–C fibres. (b) Surface microstructures of Si–B–N–C fibres. (c) Cross-section microstructure of Si–B–N–C fibres.

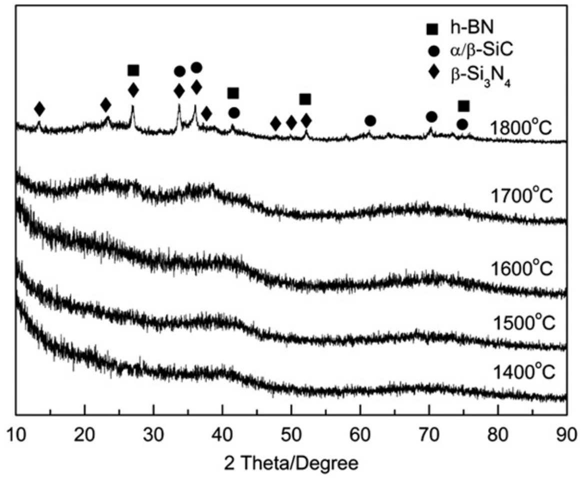


Fig. 8. XRD patterns of ground-up Si–B–N–C fibres after annealing at 1400–1800 °C in Ar atmospheres.

4. Conclusions

A soluble polyborosilazane for Si–B–N–C ceramic fibres was synthesised using a one-step condensation reaction from BCl_3, $MeSiCl_3$, and HMDS. Dehydrogenation reaction between Si–H and N–H groups did not occur and the reaction mixture did not cross-link even at the maximum reaction temperature. The polyborosilazane exhibits controlled viscoelastic properties to be readily melt-spinnable into flexible and fine green fibres with uniform diameters. The green fibres could be cured by exposing them to $HSiCl_3$ at 80 °C. As-cured fibres were pyrolyzed in a nitrogen atmosphere at 1200 °C yielding high performance Si–B–N–C fibres with average tensile strengths of 1.5 GPa and Young's modulus of 160 GPa.

Moreover, the Si–B–N–C ceramic fibres retained a fully amorphous phase up to 1700 °C. Such performance characteristics make these Si–B–N–C ceramic fibres to be excellent potential candidates for fibrous reinforcements used in ceramic matrix composites for high temperature applications.

Acknowledgements

This work was financially supported by the Exploring Project for W&E (no. 7130902), National Natural Science Foundation of China (nos. 50702075 and 51172280) and Fund of Key Laboratory of Advanced Ceramic Fibres & Composites (9140C820103110C8201).

Appendix A. Supplimentary information

Supplementary data associated with this article can be found in the online version at http://10.1016/j.ceramint.2012.05.001

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