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Ceramics International 40 (2014) 4797–4804

CERAMICS INTERNATIONAL

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Large-scale preparation of SiBN ceramic fibres from a single source precursor

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Received 27 July 2013; accepted 7 September 2013
Available online 16 September 2013

Abstract

Large-scale production of SiBN ceramic fibres was achieved by the pyrolysis of *N*-methylpolyborosilazane. This precursor was prepared by a three-step synthesis starting from hexamethyldisilazane (HMDS), silicon tetrachloride (STC), boron trichloride (BTC), and methylamine. To prove the feasibility of the synthesis on both the large and laboratory scales, the structure and composition of the as-synthesised polymer was characterised by Fourier transform infrared (FT-IR) and Nuclear Magnetic Resonance (NMR) spectroscopy and elemental analysis (EA). Differential scanning calorimetry (DSC) showed that the obtained large-scale polymer had a wide glass transition temperature range (32 °C to 50 °C) and a low transition temperature (40.41 °C), making it suitable for melt spinning. Both the large- and lab-scale synthesised polymers were successfully processed into polymer green fibres by a melt spinning process under an inert atmosphere, as the synthesised polymer is air and moisture sensitive. Endless and crack-free green fibres above 1000 m in length were successfully collected on a rotating spool, followed by cross-linking and thermolysis up to 1000 °C in an ammonia atmosphere. The SiBN ceramic fibres are amorphous up to 1600 °C in a nitrogen atmosphere. The presented results emphasise a feasible approach to highly thermally stable SiBN ceramic fibres on a large scale starting from a greatly flexible single-source precursor.

Keywords: Large scale preparation; Single source precursor; SiBN ceramic fibres

1. Introduction

The polymer-derived ceramic (PDC) route is suitable for the preparation of ceramic fibres; the main interest of this route lies in the feasibility of tailoring polymers with adjustable viscoelastic properties for the preparation of fine-diameter fibres [1–3]. SiBNC ceramics are promising candidates for high-temperature applications (oxidising or reducing environments, mechanical load, etc.) [4,5]; however, the brittleness of ceramics limits the use of ceramic fibres. Xiaolin et al. [6] were able to successfully synthesise thermally stable SiBN(C) fibres (up to 1600 °C) using polycarbosilazane (a SiCN precursor) as the starting polymer and BCl_3 as the cross-linking agent, but the process was relatively time-consuming. Later, Chu et al. [7] reported a simplified process using a mixture of polyorganosilane and polyborosilazane to produce SiBNC(O) fibres 15.6 mm in diameter with a tensile strength of 1.6 GPa. Sneddon and coworkers [8] synthesised polyborosilazanes (PBSZ) by the reaction of hydridopolysilazane (HPZ) with monofunctional boranes; these polymer precursors showed sufficient rheological properties and thermal stability, which allowed their melt spinning into fibres. Bernard and coworkers [9] reported a process of aminolysis of a single-source precursor, boron-modified polysilazane ($[B(C_2H_4SiCH_3NCH_3)_3]_n$). These polymers could be extruded into green fibres by a melt spinning process and further converted to SiBN(C) ceramic fibres through subsequent pyrolysis. The SiBN(C) ceramic fibres pyrolysed up to 1400 °C were amorphous. So far, Jansen and coworkers have been successful in the production of continuous SiBN(C) ceramic fibres [1,10]. A considerable amount of research has been conducted on the production of SiBN(C), but far less work has been reported for the preparation of SiBN ceramic

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http://dx.doi.org/10.1016/j.ceramint.2013.09.027

fibres. Tang et al. [11] reported the preparation of SiBN fibres using methyl-containing polyborosilazane as the precursor polymer; decarburisation was carried out by first curing the green fibres with a Cl-containing species and then removing the carbon content with the help of an ammonia atmosphere. In our group, we also conducted related work [12] on SiBN ceramic fibres 35 μm in diameter on a laboratory scale.

However, very little work has been reported on the large-scale production of SiBN ceramic fibres. As the large scale is inspired by the laboratory scale, thus the structure and composition of the large-scale polymer precursor was adapted from the lab scale. In the present work, we report the large-scale synthesis of a SiBN ceramic precursor and the corresponding precursor polymer using a three-step polymerisation in a tandem reactor. Continuous SiBN green fibres can be obtained through a special melt spinning apparatus. The molten spinnability of the polymer precursor and its inorganic conversion is presented. Additionally, the feasibility of the preparation of SiBN ceramic fibres on the large scale is also discussed.

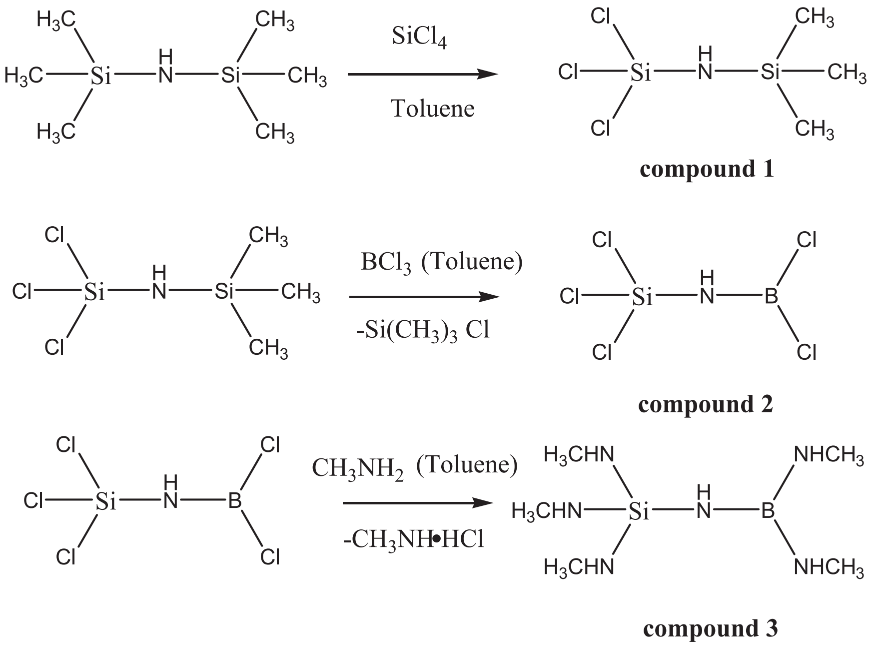
2. Materials and methods

2.1. General procedures

Silicon tetrachloride, hexamethyldisilazane (HMDS) (Acros Organics), boron trichloride (BCl_3, BTC) (Beijing Multi Technology Co.), and methylamine (CH_3NH_2) (Zhejiang Jiangshan Chemical Co., Ltd.) were used as starting materials. Methylamine was freshly stored in toluene at −40 °C before use. Toluene obtained from Sino harm Chemical Reagent Co., Ltd. was purified by distillation using potassium hydroxide under a nitrogen atmosphere. All operations were carried out under a highly purified argon atmosphere using Schlenk techniques.

2.2. The large-scale synthesis of N-methylpolyborosilazane

The synthesis of *N*-methylpolyborosilazane was carried out using the procedure reported by Jansen [1]. In a 500 L glass-lined reactor equipped with a brine–ice cooled reflux condenser, HMDS (342 mol, 55.00 kg) was dissolved in 4 L of pre-dried toluene, and then a solution of STC in toluene (400 mol, 71.20 kg) was gradually added to the HMDS solution under mechanical stirring. The reaction mixture was stirred for 24 h at room temperature. The chemical formulae of the obtained mixture (compound 1) are shown in Scheme 1. Subsequently, the solution obtained above was cooled to −40 °C, and BTC (400 mol, 49.00 kg) was slowly added over a period of 12 h. The reaction was then held at −20 °C for 12 h. The monomeric precursor trichlorosilyl-amino-dichloroborane (TADB) was obtained after stirring for 24 h at room temperature (compound 2, Scheme 1). The last synthesis step is the dechlorination of TADB by methylamine. Excess methylamine (almost 6000 mol, 192 kg) was condensed below −80 °C in a 2000 L glass-lined reactor cooled by an ice reflux condenser; TADB was transferred dropwise into the methylamine/toluene solution, and the solution was kept for 3 h at this temperature. The reaction mixture was then warmed to room temperature and stirred for several hours. The polymer solution was separated and the precipitated product was removed three times with purified toluene. After removing the toluene by distillation at 60 °C under vacuum, the polymer was obtained as a yellow, highly viscous liquid (335 mol, 68 kg) (compound 3).



Scheme 1. The synthesis of compound 3.

2.3. *The preparation of green fibres*

Polymer green fibres were prepared in a self-made nitrogen-filled spinning room, as shown in Fig. 1. Compound 3 was transferred to a 20 L agitated reactor under the protection of an argon atmosphere. The appropriate viscosity was obtained at 150 °C according to the laboratory synthesis. The molten polymer *N*-methylpolyborosilazane was extruded into green fibres through a spinneret with 0.3 mm capillaries; the fibres were collected on a rotating spool in the spinning chamber. Because the polymer and green fibres are sensitive to air and moisture, the spinning chamber was repeatedly purged by a vacuum and subsequently filled with ultra-high purity nitrogen several times to remove the residual air.

2.4. *Polymer to ceramic conversion*

The obtained green fibre was air-sensitive, so it was handled under nitrogen. The green fibres were cross-linked in ammonia at 300 °C with a heating rate of 60 °C/h, and they were kept for 3 h in a horizontal Schlenk furnace. The obtained cross-linked fibres were further heat treated at different temperatures (400 °C, 600 °C, 800 °C, and 1000 °C) using a heating rate of 60 °C/h and a dwelling time of 2 h under an ammonia atmosphere. For the high-temperature sintering of the sample pyrolysed at 1000 °C, we used a heating rate of 60 °C/h to reach the desired temperature (1400 °C or 1600 °C) under a nitrogen atmosphere in an alumina furnace.

2.5. *Characterisation*

Fourier transform infrared (FT-IR) spectra of the samples were recorded using KBr pellets on a Nicolet 8700 spectrometer in the 4000–400 cm^{-1} frequency range. ^{1}H and ^{11}B NMR spectra were recorded in $CDCl_3$ with a Bruker Avance 400 spectrometer operating at 400.13 and 128.37 MHz, respectively. Tetramethylsilane (TMS) was used as a reference. ^{13}C and ^{29}Si solid-state NMR spectra were obtained at 100.61 and 79.49 MHz, respectively, under MAS conditions. For the element composition analysis, a carbon analyser (Leco-200, Leco Corporation, USA) was applied to determine the carbon content, and an N/O analyser (Leco TC-436, Leco Corporation, USA) was used to record the oxygen and nitrogen content of the ceramic samples. Analysis of the other elements was carried out with an Elementar Vario III Analyser and a Leeman Prodigy ICP-OES. The crystalline structure was characterised by X-ray diffraction (XRD) analysis (XRD Rigaku, Tokyo, Japan) using Cu Kα radiation. Patterns were collected with a scanning step of 0.05 (2θ).

Thermogravimetric analysis (TGA) was conducted with a Netzsch 209 F1 Iris instrument. The samples were heated under a flow of nitrogen at 1 °C/min from 30 °C to 1000 °C.

The thermal properties (polymer softening and decomposition) were studied by differential scanning calorimetry (DSC, Netzsch, Germany) under a nitrogen atmosphere from 0 °C to 200 °C at a heating rate of 10 °C/min.

The morphologies of both the green fibres and SiBN ceramic fibres were characterised by scanning electron microscopy (SEM) using a Hitachi S-3000 N instrument.

The dielectric properties were measured by the perturbation method using a cavity resonator and a vector network analyser over the frequency range of 2 GHz to 18 GHz at ambient temperature.

3. Results and discussion

3.1. *Large-scale synthesis*

The molecular precursor containing the functional group Si–N–B can be synthesised starting from hexamethyldisilazane.

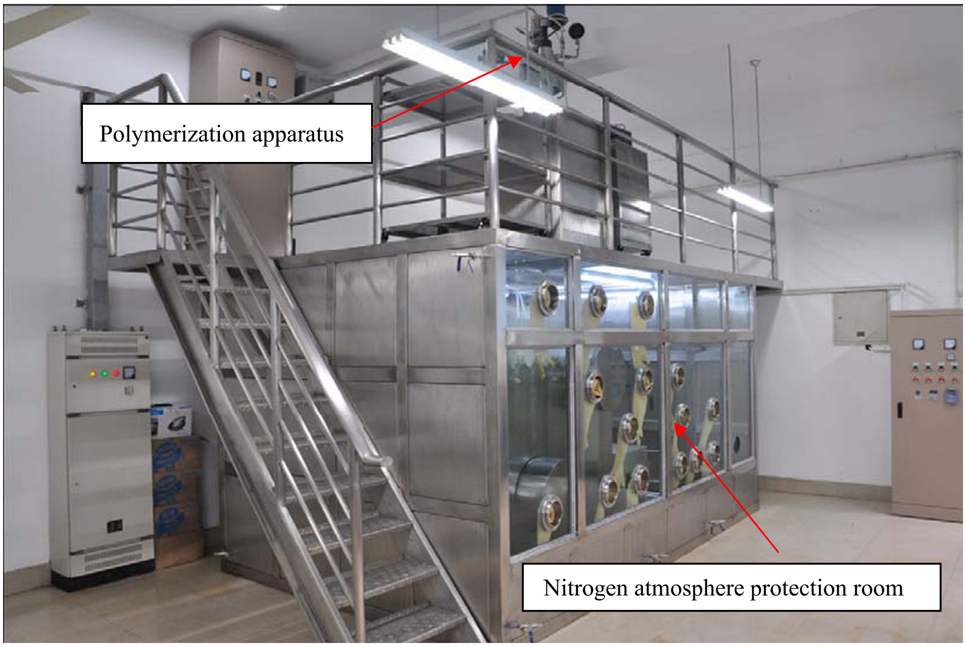


Fig. 1. Large-scale melt spinning apparatus filled with a nitrogen atmosphere.

Such a structure is obtained by the substitution of only one trimethylsilyl group of hexamethyldisilazane by silicon tetrachloride and the subsequent elimination of the second trimethylsilyl group by the reaction with boron trichloride [1].

The chemical composition and structure of both the lab-scale and large-scale synthesised polymers were investigated by FT-IR and NMR spectroscopy. As shown in Fig. 2(a) and (b), both spectra show similar stretching and deformation bands. The weak signals at 2954 cm^{-1}, 2890 cm^{-1}, and 2813 cm^{-1} are caused by C–H stretching; the signal from the N-bonded C–H at 2813 cm^{-1} is marked. The broad peak at 3428 cm^{-1} is attributed to N–H stretching. The band assigned to N–H bond deformation in the –NHCH$_3$ end groups is located at 1596 cm^{-1}, and the concurrent stretching vibration of the NCH$_3$ units are found at 1073 cm^{-1}. The particularly strong signal at 928 cm^{-1} is caused by the stretching vibration of the Si–N linkage. The characteristic peak of B–N is visible at 1349 cm^{-1}, suggesting the presence of a Si–N–B bridge [13].

Moreover, some signals in the NMR spectra are helpful in determining the structure of the polymer precursors. The ^{11}B, ^{13}C, and ^{29}Si solid-state NMR spectra (Fig. 3) of the large-scale polymer are very similar to those of the lab-scale polymer. In the ^{11}B NMR spectrum, a signal in the region of tri-coordinate boron atoms, located at 27 ppm, is attributed to the BN$_3$ site; the signal at 55 ppm is diminished due to the conversion from B–N(H)–CH$_3$ to B–N(CH$_3$)–CH$_3$. The transformation of the structure can be confirmed by ^{13}C NMR spectroscopy; both the lab-scale and large-scale synthesised polymers show two signals at 1.08 ppm and 27.5 ppm, which are assigned to N–CH$_3$ and NH–CH$_3$, respectively. To obtain more information concerning the N atom connectivity with the Si and B atoms, ^{29}Si NMR spectra were recorded, which show two signals at −32.9 ppm and −50 ppm, which are assigned to SiCN$_3$ and SiN$_4$ for both samples, respectively. The presence of SiCN$_3$ suggests the formation of Si–N–B due to the elimination reaction of methylamine between Si–NHCH$_3$ and B–NHCH$_3$. On the other hand, the SiN$_4$ structure is probably a six-membered Si–N ring formed via polycondensation. There are some differences in the ^{1}H NMR spectra of the lab- and large-scale polymers, but there is still a similar peak contribution. The sharp signal at 0.1 ppm in both samples is caused by the reference Si–CH$_3$ site, and the resonance peak at 2.4 ppm in both samples represents the presence of N–CH$_3$. However, it is noted that the two broad peaks at 0.6 ppm and 0.8 ppm only appear in the lab-scale synthesised polymer; unfortunately, we have not been able to identity which group these peaks belong to. In summary, the structure of the polymer precursor derived from the large scale is similar to that synthesised on the lab scale, demonstrating that the large-scale synthesis is a feasible approach. The structure consisted of SiN$_4$ six-membered rings connected by –NH–B and N(CH$_3$)$_2$–B units.

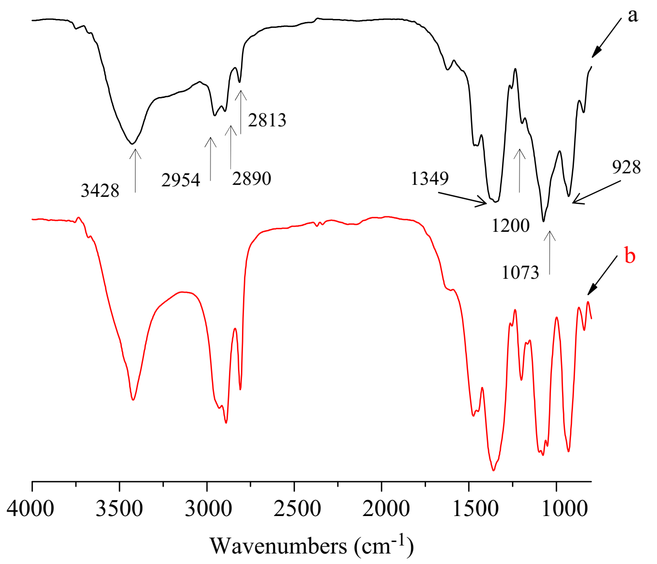


Fig. 2. FT-IR spectra of *N*-methylpolyborosilazane: (a) large-scale samples and (b) lab-scale samples.

3.2. Melt spinning investigation

The melt spinnability of *N*-methylpolyborosilazane was investigated by differential scanning calorimetry (DSC) (Fig. 4). The glass transition (T_g), which covers approximately 20 °C, was observed from 32 °C to 50 °C. This wide range of the glass transition probably results from the high molar mass distribution in the polymer [14]. On the other hand, a low softening temperature was observed, close to room temperature, indicating that *N*-methylpolyborosilazane is a qualified candidate for stretchable polymer filaments [15]. It is formation of terminal groups such as N(H)CH$_3$ that leads to the mobility of the polymer chains. The presence of the N(H)CH$_3$ end group in our large-scale polymer precursor was confirmed by preliminary FT-IR and NMR spectroscopy. As expected, the *N*-methylpolyborosilazane obtained by the large-scale synthesis can successfully be transformed into a spinnable molten polymer. Endless green fibres with a diameter of 40 μm were continuously collected on a rotating spool by stretching the filament emerging from the spinneret at a relatively high spool velocity with capillary stability (see Fig. 5). Additionally, SEM (Fig. 6) showed that the green fibres were smooth and crack free.

3.3. Inorganic conversion

The thermal stability of the polymer precursor was evaluated using thermogravimetric analysis (TGA) upon heating to 1000 °C in a nitrogen atmosphere (Fig. 7). The larger scale of the reaction has no significant effect on the ceramic yields. The ceramic yield of the samples synthesised on the large scale is 3.7 wt% higher than that of the lab scale synthesis, (65 wt %). The mass loss has been divided into three stages; the first step occurs at 275 °C (approximately 10% weight loss). The mass loss of the polymer synthesised on the large scale is much higher than that of the polymer synthesised on the lab scale; in fact, no mass loss is observed in the lab-scale sample. Generally, initial decomposition is caused by the loss of solvent and volatile components. The difference between the

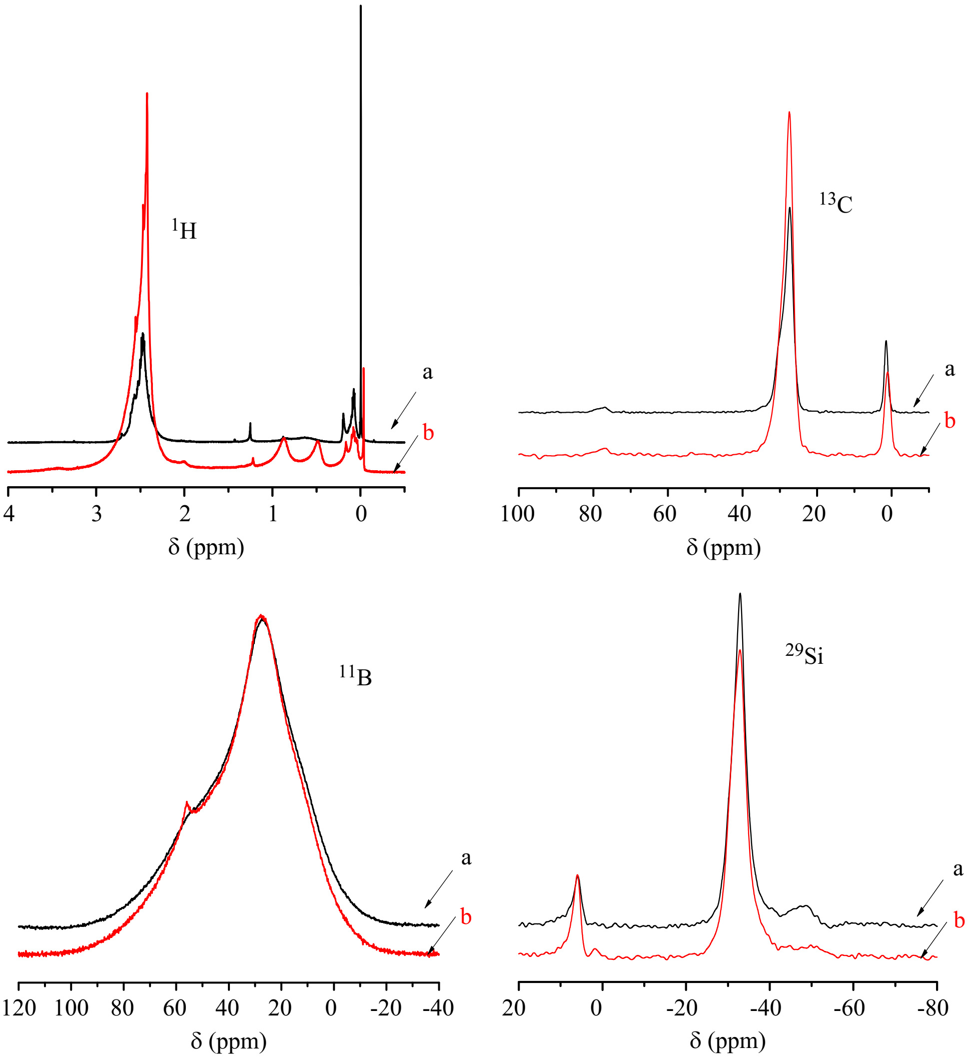


Fig. 3. NMR spectra of *N*-methylpolyborosilazane: (a) large-scale samples and (b) lab-scale samples.

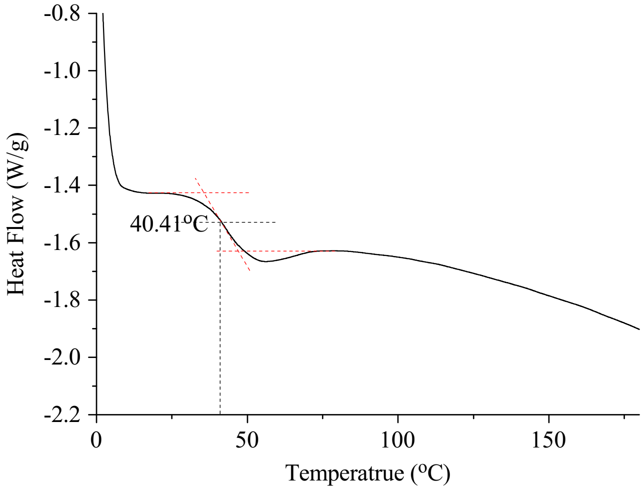


Fig. 4. DSC curve of *N*-methylpolyborosilazane (large-scale polymer).

lab-scale and large-scale synthesis is the amount of added methylamine. In the case of the large-scale synthesis, excess methylamine is used to dissolve chloride (methylamine) precipitates; hence, this difference in the initial decomposition can be attributed to the volatilisation of excess methylamine. A further mass loss of 10% occurs between 300 °C and 450 °C, due to the partial sublimation and decomposition of organic oligomers, which overlap. At higher temperatures, from 450 °C to 600 °C, the observed mass loss of 25% is attributed to the polymer conversion into the inorganic ceramic. During this process, methane or its fragments are lost from terminal methyl groups, and hydrogen elimination also occurs [16]. Meanwhile, as shown in Table 1, the carbon content is dramatically reduced by 17% during the process of converting the green fibres to inorganic fibres (600 °C), due to the elimination of terminal methyl groups. In addition, a tiny weight loss (approximately 1.5%) was observed between 600 °C and 1000 °C, and the ceramic yield at 1000 °C was 63.7 wt%.

Previous research has indicated that boron content in the region from 5% to 17% is able to provide remarkably high temperature stability [17–19]. The higher the boron content present in the ceramic, the easier the structure is transformed into the crystalline state. The boron content of SiBN ceramic fibres prepared in the present work is in the effective range (10.5 wt%), so it should display a high temperature stability. Further investigation of the crystalline behaviour was performed by XRD (Fig. 8). Cured fibres or pyrolysed fibres at different temperatures exhibited an amorphous structure, revealing the high temperature stability of our SiBN fibres (up to 1600 °C).

Prior to the pyrolysis of the green fibres, the critical step is their cross-linking so that they can retain their integrity during the inorganic conversion. Owing to the high chemical reactivity of the precursor with ammonia, which can improve the compactness of ceramic fibres [16], the green fibres were exposed to a flow of ammonia in our cross-linking step. The morphology of the fibres pyrolysed at different temperatures was observed by SEM. As shown in Fig. 9, the cured fibres developed tiny holes upon heating at 300 °C and are finer in contrast to the green fibres (Fig. 9a). The volume of the cured fibres decreases as the pyrolysis temperature increases. Further dehydrogenation and transamination reactions lead to the rearrangement of the structure and the elimination of organic molecules, such as methylamine, methyl end groups, and hydrogen. This leads to the observed decrease in the volume and porosity and enhances the densification. Hence, the ceramic fibres that were pyrolysed at 1000 °C showed smooth surfaces and structural uniformity. Upon annealing at 1600 °C, the morphology of the ceramic fibres retains its integrity; thus, final ceramic fibres with diameters in the range of 25–30 μm were obtained. At room temperature, the filament tensile strength of the SiBN ceramic fibres as-pyrolysed up to 1600 °C is 0.512 GPa, which is the average value from 20 measurements.

The dielectric properties of our SiBN ceramic fibres obtained at a temperature of 1600 °C were examined, and it was found that they demonstrated a very low dielectric

Fig. 5. The filament bobbin of the *N*-methylpolyborosilazane green fibres.

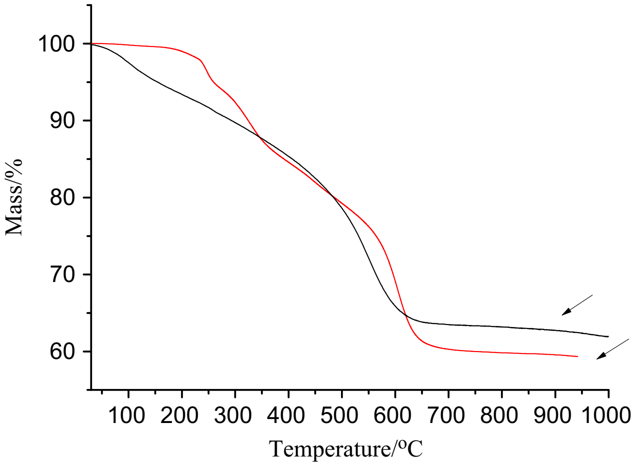


Fig. 7. TGA curves of *N*-methylpolyborosilazane: (a) large-scale samples and (b) lab-scale samples.

Table 1
Elemental composition of the *N*-methylpolyborosilazane green fibres and ceramic fibres pyrolysed at different temperatures.

Samples	Si	B	N	C	H	Empirical formula ceramics
SiBN_Green	26.9	5.3	32.3	27.4	8.1	–
SiBN_400 °C	29.2	8.2	37.7	18.5	6.4	–
SiBN_600 °C	33.3	9.9	40.1	10.4	6.3	–
SiBN_1000 °C	39.9	11.9	42.9	3.7	1.6	$Si_{1.2}BN_{2.57}C_{0.26}H_{1.34}$
SiBN_1600 °C	44.1	10.5	44.9	<0.1	0.2	$Si_{1.5}BN_{3.1}$

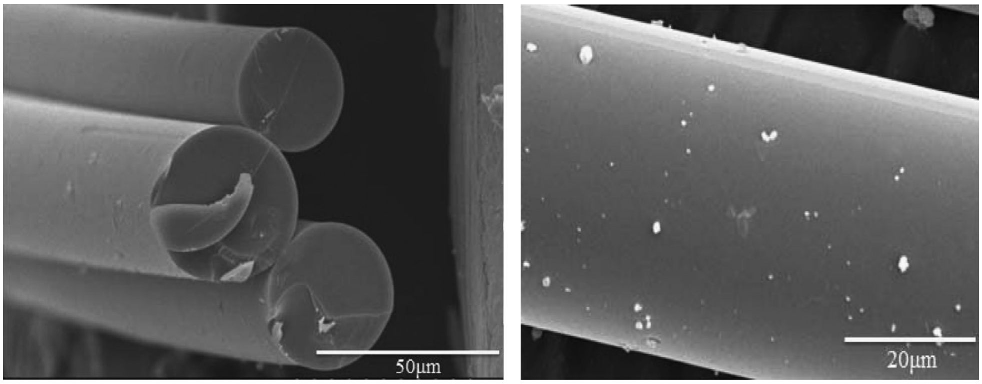


Fig. 6. SEM images of the *N*-methylpolyborosilazane green fibres.

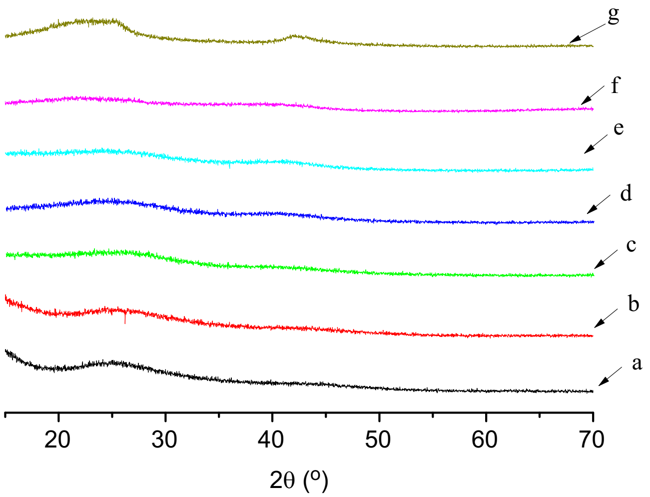


Fig. 8. XRD patterns of *N*-methylpolyborosilazane pyrolysed at different temperatures. (a: 200 °C; b: 400 °C; c: 600 °C; d: 800 °C; e: 1000 °C; f: 1200 °C; and g: 1600 °C).

constant (ε') of 2.61 and a loss tangent ($\tan\delta$) of 0.0027 ($f = 10$ GHz) at ambient temperature, which is lower than that of previously reported quartz fibres (3.12 and 0.0036, respectively) [11]. This result could be attributed to two important factors: one is the extremely low carbon content (<0.1 wt%, as shown in Table 1), which favours a decreasing dielectric value, and the other is a consequence of the nearly stoichiometric composition, which shows that $Si_{1.5}BN_{3.1}$ pyrolysed at 1600 °C is represented by $(Si_3N_4)_{0.5}(BN)N_{0.2}$. Therefore, SiBN ceramic fibres with a low carbon content prepared on the large-scale could potentially be useful for applications in microwave-transparent systems.

4. Conclusions

The large-scale synthesis of *N*-methylpolyborosilazane was realised by a continuous three-step reaction starting from $SiCl_4$, HMDS, BCl_3, and $MeNH_2$. This precursor favoured

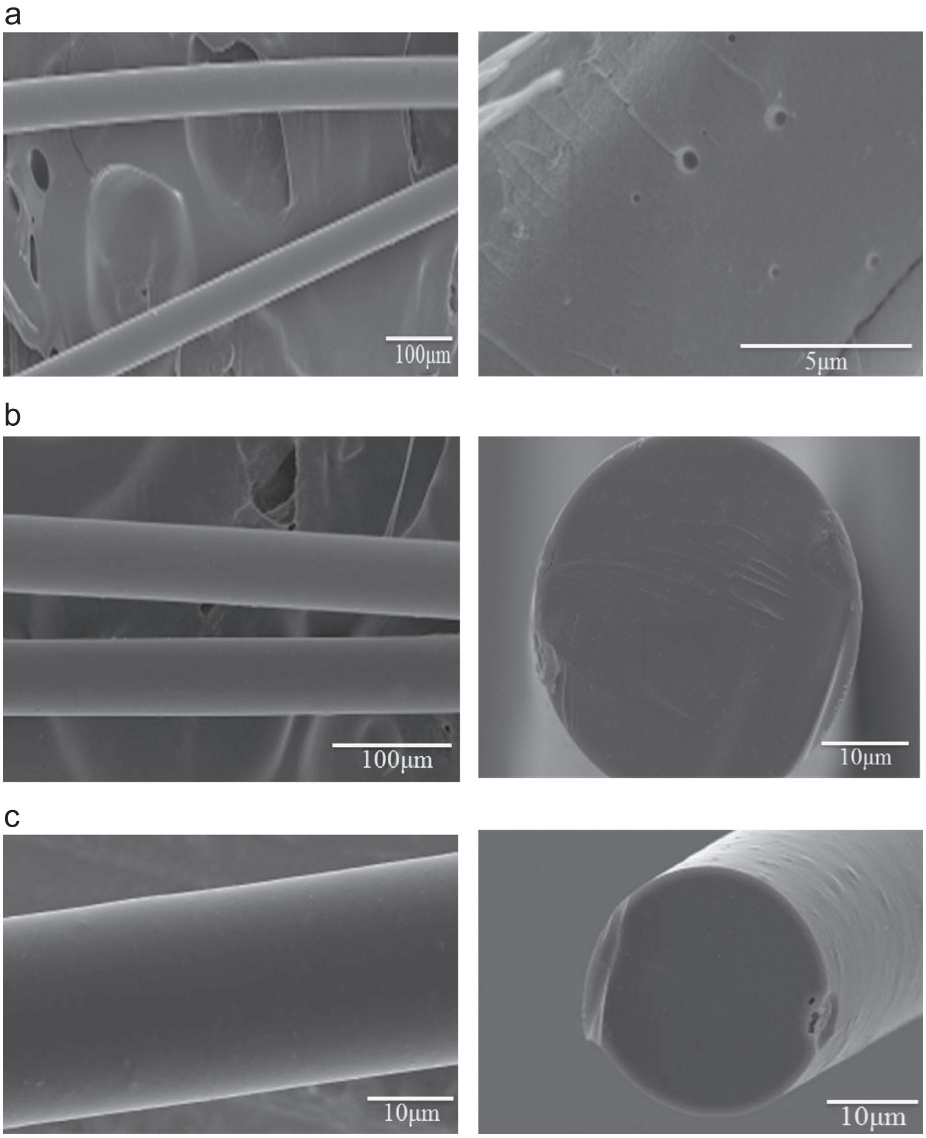


Fig. 9. SEM images of the *N*-methylpolyborosilazane pyrolysis products at different temperatures (a: 300 °C; b: 1000 °C; and c: 1600 °C).

the fabrication of continuous green fibres and ceramic fibres. The structure of the polymer precursor via the large-scale synthesis is similar to that derived from the lab-scale synthesis, with six-membered SiN_4 rings connected by –NH–B and $N(CH_3)_2$–B units. Additionally, *N*-methylpolyborosilazane synthesised on the large scale exhibited excellent spinnability, and continuous green fibres were obtained via self-made melt spinning equipment. Green fibres and SiBN fibres pyrolysed at 1600 °C are uniform, smooth, and crack-free. The combination of amorphous structure, excellent dielectric properties, and high temperature stability suggest these fibres as promising materials in radar-wave-transparent applications. Also, their mechanical properties may be improved by applying a tension force during the pyrolysis, which may make it possible to use these SiBN ceramic fibres as reinforced materials in composites.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (Grant no. 90916025).

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