

Preparing continuous SiBN ceramic fiber from Precursor Polymer of N-methylpolyborosilazanes

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1 General Introduction

The high speed aircrafts and supersonic near space vehicle require high temperature-resistance ceramic materials for electromagnetic windows or radomes to meet the stringent requirements of higher speed, higher temperature, and longer flight times. Such materials must have low density, high thermal stability, and a low dielectric constant across hundreds of centigrade and high mechanical performance^[1-3]. However, the brittleness of ceramic materials limit its use as a large engineering component, and continuous fiber reinforced ceramic is an effective route to overcome this problem. Therefore, the preparation of ceramic fiber with good electromagnetic properties, mechanical properties, and thermal properties is the key issue for such materials^[4-6].

Some of commercial ceramic fiber, such as quartz fibers, Si₃N₄ fibers and BN fibers^[7] are considered to use for such applications, and each of these fibers has its individual advantage in properties. However, these fibers cannot meet such comprehensive properties. Therefore, it is important to create a material to meet high temperature, radar-wave-transparent, lightweight and strong applications. which can keep the dielectric, mechanical properties, and thermal stability balance.

SiBN fiber is a new type of ceramic fibers, that expected to possess such comprehensive performances with high mechanical properties, good dielectric behaviors, and excellent thermal resistance. Therefore it is considered as the best candidate for reinforcement in high-temperature, radar-wave-transparent

ceramic composites.

Xiao et al^[8] has firstly reported on the preparation of SiBN fibers. They used methyl-containing polyborosilazane as the preceramic precursor for the SiBN ceramic fiber. The decarburization was carried out by curing the green fibers with Cl-containing species, which can preliminarily reduce the carbon content through loss of the organic groups, and further by pyrolyzing the cured fibers in ammonia atmospheres.

Another similar ceramic fiber containing Si/B/N elements is SiBNC fibers, which have been prepared from many types of polyborosilazane. Martin Jasen and co-workers^[9] have done a lot of works in this field, and obtained lots of remarkable fruits. They prepared N-Methylolyborosilazanes by aminolysis of trichlorosilylamino-dichloroborane(TADB) via a monomer route. polyborosilazanes can be tailored to be meltable and spinnable by melt- or solution-spinning process.

We have developed a new route to prepare SiBN fiber from precursor polymer by copolycondensation of B(NHCH₃)₃ and Si(NHCH₃)₄, the advantage of this new route is easy to tailor the material structure by adjusting the ratio of monomers. another advantage is that both monomers are easy to synthesis and are commercial available raw materials, which will greatly reduce the cost of production.

2 Experimental

2.1 Materials

All solvents were dried and purified using standard procedures and were freshly

distilled under nitrogen from calcium hydroxide (CaH_2) prior to use. Tetramethylsilane (SiCl_4) and Hexamethyldisilazane $\{[(\text{CH}_3)_3\text{Si}]_2\text{NH}$, HMDS} were obtained from ACROS ORGANICS in 98% purity, boron trichloride (BCl_3) was purchased from Beijing Multi Technology Co., Ltd and all of them were directly used without further purification. Methylamine (CH_3NH_2) solution was slowly condensed into toluene at -78°C for further use. Argon (Ar) and nitrogen (N_2) were used as received (>99.999%). Monomer which was made by above materials was stored and filtered in a glove box for further polycondensation.

2.2 Synthesis of Polyborosilazane (PBSZ)

Monomer $((\text{CH}_3\text{NH})_3\text{SiNHB}(\text{NH}_2\text{CH}_3)_2)$ was obtained through the reaction of SiCl_4 , HMDS, BCl_3 and CH_3NH_2 solution under N_2 protection. The reaction process was described by our previous papers (Fig.1)^[5]. Then $(\text{CH}_3\text{NH})_3\text{SiNHB}(\text{NH}_2\text{CH}_3)_2$ was put in a 500ml three-necked flask placed in an argon-filled glove box. The monomer was heated to 100°C for 1h at a heating rate of $5^\circ\text{C}/\text{min}$ with vigorous stirring, then the solvent was evaporated under 120°C for 2h. Finally, the polymerization temperature was heated to 150°C for 48h under argon atmosphere. The PBSZ polymer was obtained as a viscous fluid and were stored into an argon-filled glove box. The process of polycondensation was shown in Fig.2.

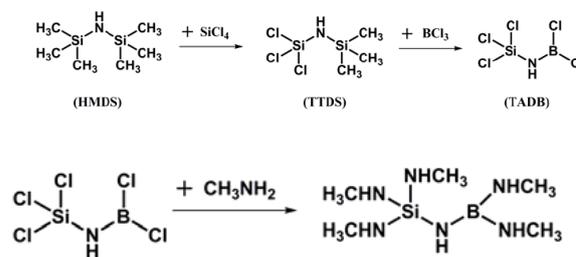


Fig.1 Synthesis of monomer

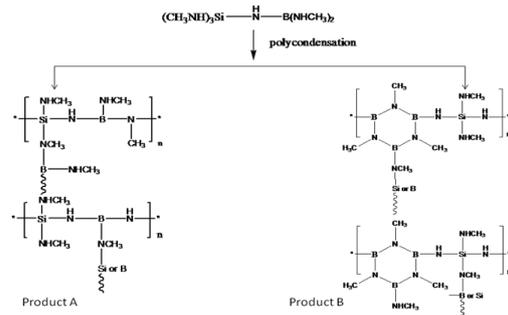


Fig.2 Synthesis process of PBSZ

2.3 Rheological Test of Polyborosilazane (PBSZ)

Polymers were handed into round slice inside an nitride-filled glovebox, Rheological measurements were carried out at ARES-RFS(TA.Co. USA) with a coaxial parallel plate geometry having a diameter of 25 mm, The gap was adjusted to 0.5mm, 0.5g of samples were placed preheated fixture plates located in nitrogen ambience and then heated to the spinning temperature (T_{spinning}). Dynamic shear tests were executed in the linear viscoelastic region obtained by strain sweep test at 130°C , using controlled strain amplitude ($\gamma_0=10\%$), The storage modulus G' , the loss modulus G'' and complex viscosity η^* were obtained from the dynamic shear measurements.

2.4 Melt Spinning

The spinning was performed on a self-made spinning machine equipped with gear pump, godet roller and spinning winder, which was put in spinning room filled with inertia atmosphere.

2.5 Characteration

FT-IR spectra were obtained with a Nicolet 8700 spectrometer as KBr pellets. ^{11}B and ^{29}Si solid state NMR spectroscopy were performed using a Bruker Avance 400 spectrometer operating at 100.62 and 79.49 MHz, respectively under MAS conditions. Rheological properties was shown by Dynamic shear tests at ARES-RFS(TA.Co. USA). Green fiber morphology was observed by scanning electron microscopy (SEM), Hitachi S-3000N. The cross section as well as the surface of the fibers were investigated.

3 Result and Discussion

3.1 Structure analysis

The structure of precursor was investigated

by NMR and FT-IR spectroscopy. In the ^{29}Si solid-state CP MAS-NMR spectrum (Fig.3), appearing two single peak at -32ppm and -90ppm correspond to Si-N and Si-O respectively, in which a broad signal is present at -32ppm match with Si-N-B in consistence with the document. The sample is sensitive to air and moisture, Si-O bond can emerge easily in the test process. One broad signal appeared at 27.5ppm and the weak signal at about 56ppm may be contributed to BN protons in and out B-N₃ hexatomic ring respectively in ^{11}B NMR spectrum .

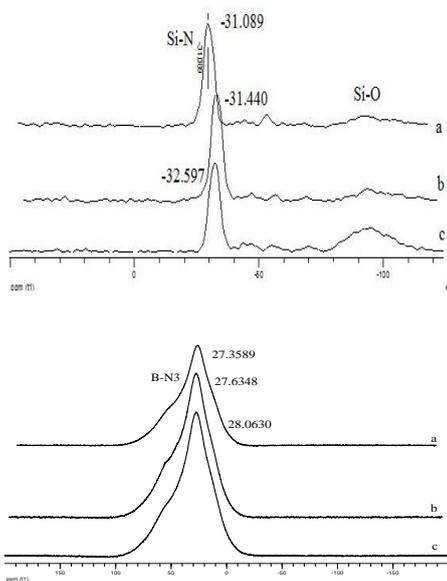


Fig.3 ^{29}Si NMR and ^{11}B NMR of PBSZ at different polymerization times at 150⁰C
a)48h; b)36h; c)24h

The IR spectrum (Fig.4) displays the characteristic stretching and deformation bands of all expected motifs. All precursor pose similar spectrum among 24h on 48h. The series of weak absorption signal for the N-H stretching modes in the 3425cm⁻¹ confirm the presence of the NHCH₃ ending group in the polymer structure, which shows common structure characterization in the Product A or B. The intensive absorptions appeared at 2960 cm⁻¹ can be attributed to C-H stretching vibrations. B-N vibrations are visible at 1386cm⁻¹. Moreover, absorptions at 710cm⁻¹ indicated the presence of direct B-N links and the rings linked through -N(CH₃)- bridges. Si-N-Si

vibrations were shown at 894 cm⁻¹ [10], whereas those of Si-N units appear around 948 and 1051 cm⁻¹ [11]. Si-O bonds that may format during the test gave attribution to the absorptions at 950 and 1100 cm⁻¹.

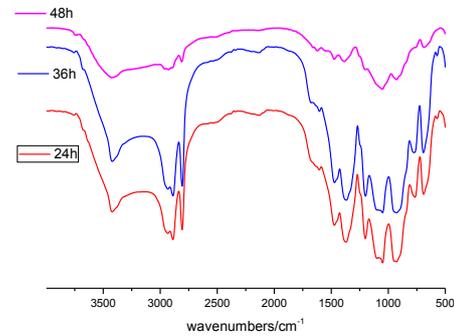


Fig. 4 FT-IR of PBSZ at different polymerization times at 150⁰C

3.2 Melt spinnability research

According to Sylvain Duperrier [12] Measurements of the viscosity and elasticity of molten polymers at their spinning temperature is important for controlling the melt-extrusion process and the subsequent drawing of the derived molten filament, which could be investigated by Rheological test. The frequency dependence of the rheological parameters was determined during dynamic frequency sweep experiments within the LVE range. As-potted curves (Fig.5) displaying the frequency dependence of the storage modulus G' , the loss modulus G'' , and the complex viscosity η^* for the molten polymer at 110⁰C guide us to predict the melt-spinnability of PBSZ polymer.

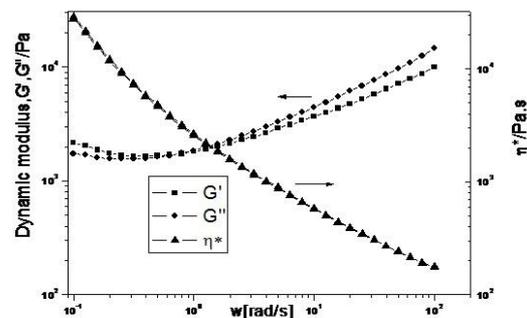


Fig.5 Oscillatory frequency dependence of G' , G'' , and η^* tested at 110⁰C about PBSZ

From the literature ^[13]. Firstly assuming the Cox-Merz relation to be applied, Then we suppose that ω is related to the shear rate within the capillary, Therefore, we propose that oscillatory frequency is proportion to a certain extent to extrusion velocity. As shown in the Fig 5, It should be noticed that the complex viscosity η^* continuously decreased, demonstrating clearly the shear-thinning behavior of PBSZ. Hence, PBSZ is a non-Newtonian fluid compound to meet the requirements of melt-spinnable polymers. At the same time, It can be seen that a crossover of G' and G'' occurs at about 0.7 rad/s, and the viscous component G'' dominate in the sequent polymerization and structure of precursor compared with elastic component (G').

Above results indicate PBSZ has excellent melt-spinning behavior at 110⁰C.

3.3 The Morphology of PBSZ Green Fiber

It is observed that PBSZ green fibers are smooth, uniform, and free of voids by SEM (Fig.6), Typical fibers were less than 35 μ m in diameter. The pictures from Fig.7 show these fibers are flexible.

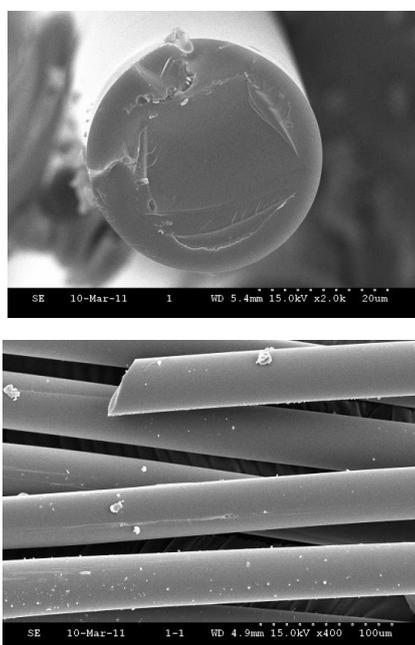


Fig.6 SEM of PBSZ green fiber



Fig.7 The photo of as-spun green fiber

4 Conclusion

Because of its chemical structure and rheology properties, The novel precursor polymer is melt-spinnable, we can obtain less than 35 μ m green fiber, which is smooth and uniform. It could be chosen to prepare SiBN ceramic fiber. From melt spinning, we are convinced that linear structure of the polymer is dominating, but the preparing of SiBN ceramic fiber should be further explored, especially how to improve stability of melt spinnability, polymer process, then investigated polymerization mechanism to come to why it is linear structure.

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