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Nearly stoichiometric BN fiber by curing and thermolysis of a novel poly[(alkylamino)borazine]

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Abstract

Boron nitride (BN) fiber with a composition of $BN_{1.09}$ was fabricated by curing and thermolysis of a novel poly[(alkylamino)borazine]. The processes have been studied by a combination of gel-content test, TGA, elemental analysis, IR, XPS, XRD, SEM and TEM. The results show that curing made polymer fiber infusible and resulted in a significant improvement of ceramic yield from 53.2 wt% to 73.8 wt% at 1000 °C. Moreover, pyrolysis in NH_3 at 1200 °C generated a nearly stoichiometric BN without carbonaceous impurities while in Ar led to a BNC material with carbon content of 6.13 wt%. The obtained amorphous BN fiber with a diameter of 13 μm displayed a tensile strength of approximately 600 MPa. Furthermore, the BN fiber illustrated good oxidation resistance in air.

Keywords: Preceramic polymer; Curing; Pyrolysis; Boron nitride fiber

1. Introduction

BN has been researched intensively due to its low density, high melting point, excellent oxidation resistance and low dielectric constant, etc. [1–5]. Considering its superior properties, BN fiber can be regarded as a promising reinforcing agent used in BN matrix composites for application in high temperature and electromagnetism environments [5–7]. Nonetheless, it is difficult to obtain BN fiber with a homogeneous composition and stable properties by traditional powder sintering and high temperature nitruration routes [1,8,9]. As a consequence, the urgent demand for high performance BN fiber makes the fabrication an attractive challenge.

The polymer-derived ceramics (PDCs) technique plays an important role in preparing shaped non-oxide ceramics such as fiber, film and porous material from soluble and fusible polymers [6,8,10–17]. The innovative idea behind this method is that the atomic structure of the final material is designed by the atomic composition and the structure of the preceramic polymers [18]. As evidenced by numerous investigations, the most promising technique to prepare BN fiber is the PDCs route [2,5–7,10,17]. Asymmetric alkylaminoborazines (AABs) were proved to be attractive molecular precursors but yet inconvenient to handle the reaction between B-trichloroborazine (TCB) and alkylamines accurately under mild conditions [5,6,19]. To facilitate the synthesis, we adopt propylamine/methylamine and TCB to fabricate a novel asymmetric AAB monomer and obtained corresponding polymeric precursor (named as PPAB) with tunable processibility. One major advantage of this technique is the facile synthesis without extraordinarily low temperature, which enables low-cost and large-scale production. Thus, the fabrication of BN fiber with low dielectric constant was initiated [5].

In this contribution, we report the successful development of a nearly stoichiometric BN fiber by spinning, curing and thermolysis of PPAB. The influence of curing and pyrolysis atmosphere on the fiber gel content, ceramic yield and chemical composition was investigated. The phase composition, microstructure and oxidation resistance of as-obtained BN fiber were also characterized.

2. Experimental

The synthesis of PPAB was described in our previous work [20]. The PPAB was spun in N_2 using a lab-scale melt-spinning

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apparatus set up in a glove-box and the resulting fiber was subsequently stretched and collected on a rotating spool. And then the spun fiber was cured in NH_3. After curing, the fiber was pyrolyzed to 1200 °C in NH_3 to yield off-white ceramic fiber. Further crystallization of the fiber was conducted in Ar.

The gel content in the cured fiber was measured by Sohex extractor with xylene as eluent. TGA was conducted on a NETZSCH STA 449C instrument in Ar or air at a heating rate of 10 °C/min. Boron content was measured by a chemical titration method. Element contents of N, O, H and C were checked by Leco TCH-600 N/H/O and Leco CS-600 C/S analyzers. IR spectra were recorded on a Nicolet Avatar 360 spectrophotometer in KBr pellets. XRD patterns were obtained using a powder X-ray diffractometer (Siemens D-5005, Cu Kα radiation). The surface of the fiber was analyzed by using a scanning electron microscope (JEOL, JSM-6300). The tensile strength was determined from failure tests performed on 30 filaments with a gauge length of 25 mm by using the statistical approach of Weibull [21]. The XPS spectra were obtained by means of a VG ESCALAB MKII instrument (Al Kα excitation). The HRTEM image was taken with a Philips CM 200 transmission electron microscope operated at 200 kV.

3. Results and discussion

3.1. Gel content and ceramic yield of cured fiber

To avoid fiber inter-fusion, spun fiber was cured in NH_3 for a while before thermolysis. The gel content was used to evaluate the fiber degree of crosslinking. The fiber gel content was plotted as a function of curing temperature, as shown in Fig. 1. Obviously, when temperature was raised from 25 °C to 70 °C, the gel content of cured fiber was enhanced from 31.8 wt% to 94.8 wt%, indicating that the gel content was influenced by temperature greatly. After curing above 60 °C, green fiber became infusible which enabled its subsequent thermolysis in NH_3.

The effect of curing on the ceramic yield of cured fiber in Ar was also investigated and plotted as a function of temperature (Fig. 2). It is clear that most of the weight loss took place below 500 °C for both cured and uncured samples. However, cured

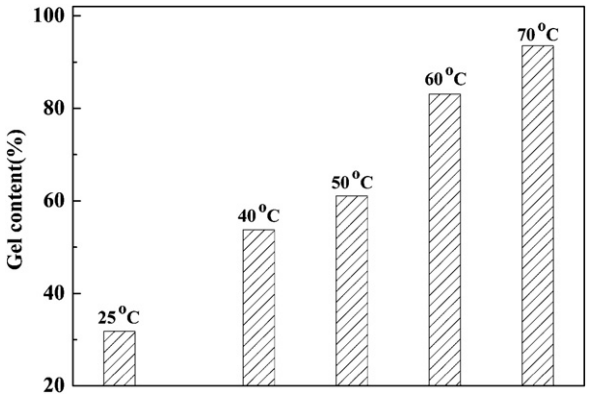


Fig. 1. Gel content of cured fiber obtained at different temperatures.

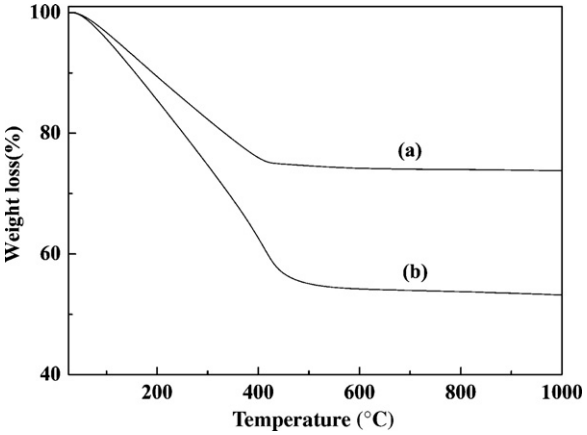
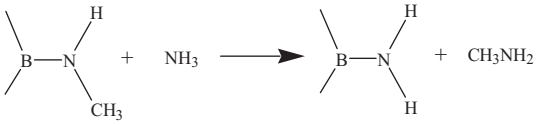
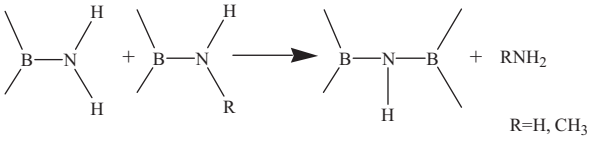


Fig. 2. TGA curves of (a) cured and (b) uncured fiber in Ar.

fiber displayed a higher ceramic yield of 73 wt% over uncured (53 wt%) at 1000 °C, suggesting that the ceramic yield of green fiber was significantly enhanced after curing [22]. It is believed that the =B–N(CH_3)– structure in polymeric precursor reacted with NH_3 according to an amine exchange pathway to form =B–NH–B= unit, as illustrated in Eq. (1) and Eq. (2) [23]. The amine-exchange reaction occurred to form highly interlocked backbones making green fiber infusible and insoluble. As a result, only a few low weight molecules escaped out, in favor of improving the ceramic yield and decreasing of voids on the surface of fiber [24]. A detailed investigation on the curing mechanism is still underway.





3.2. Influence of pyrolysis atmosphere

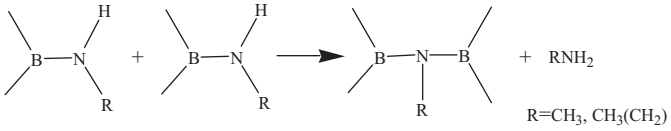
As known from previous studies [18,22,23], the composition of pyrolytic residues was influenced by atmosphere greatly. Carbon element in precursor can be easily removed by pyrolysis in NH_3. Hence, both NH_3 and Ar were used to investigate the effect of atmosphere on the composition of pyrolytic products, as listed in Table 1. It was clear that the carbon content decreased from 22.67 wt% to 18.79 wt% after curing in NH_3, indicating that the curing was favorable for carbon removal. Moreover, the N/B atomic ratio (1.25) in R–Ar was slightly higher than that in R–NH_3 (1.09). And considerable amounts of carbon remained in R–Ar whereas most of carbonaceous impurities in R–NH_3 were driven off.

Table 1
Chemical composition of the pyrolytic products at 1200 °C.

Samples	Composition (wt%)					Empirical formula
	B	C	N	O	H	
Polymer fiber	23.13	22.67	44.70	0.97	8.33	$BN_{1.49}C_{0.88}H_{3.86}O_{0.03}$
Cured fiber	25.12	18.79	45.16	0.82	8.04	$BN_{1.39}C_{0.67}H_{3.43}O_{0.02}$
R–NH_3	41.08	0.14	57.79	0.53	0.20	$BN_{1.09}O_{0.01}H_{0.05}$
R–Ar	32.54	6.13	52.74	2.45	1.10	$BN_{1.25}C_{0.17}O_{0.05}H_{0.37}$

R–NH_3 and R–Ar are products pyrolyzed in NH_3 and N_2, respectively.

The smooth carbon removal was mainly due to the condensation reactions between alkylamino units and between alkylamino units and NH_3 according to Eq. (2) [3]. The carbothermal reaction of carbon with NH_3 was also existent, as shown in Eq. (4).



$$3C + 4NH_3 \rightarrow 3CH_4 + 2N_2 \quad (4)$$

Then, the pyrolysis behavior of cured fiber in NH_3 was further studied in order to obtain BN fiber without carbonaceous impurities. The weight loss during pyrolysis was recorded and plotted in Fig. 3. As seen, most of the weight loss happened below 800 °C and the pyrolysis process can be divided into three steps [22]: (i) further crossslinking of cured fiber and evolution of low molecular weight oligomers below 400 °C with a weight loss of 11.6 wt%, (ii) formation of three-dimensional polymeric network from 400 °C to 800 °C with a weight loss of 26.5 wt%, and (iii) achievement of polymer-to-inorganic transition at 800 °C and occurring of crystallization above 800 °C with only 1.6 wt% weight loss. The ceramic yield was about 60 wt% at 1200 °C.

Fig. 4 displays the evolution of carbon content in cured fiber during pyrolysis. Prior to pyrolysis, the carbon content was 18.79 wt%. As temperature increased, it decreased drastically and most of carbon was removed below 600 °C. Above 600 °C, carbon content decreased slower and reduced to 0.14 wt% at 1200 °C. With very low carbon content and nearly stoichiometric composition, the BN fiber is deemed to possess low dielectric constant and find application in wave transparent composites [5,25].

3.3. Structure and composition of as-prepared BN fiber

The XRD patterns of BN fiber obtained at different temperatures are shown in Fig. 5. The fiber obtained at 800 °C only gave two broad diffuse peaks at around $2\theta = 25.7°$ and $2\theta = 42.6°$, revealing its amorphous nature. In the sample prepared at 1200 °C, two peaks at $2\theta = 26.3°$, 42.3° assigned to the (0 0 2) and (10) reflections of turbostratic BN (*t*-BN) [2] were observed. Further crystallization of the BN fiber in Ar occurred at 1400 °C, diffraction assigned to the (0 0 2) plane became sharper and a diffuse hump located at around $2\theta = 76°$ ascribed to the (1 1 0) diffraction was noticed, indicating higher crystallinity. However, Fig. 5(c) shows no resolution of the (1 0 0) and (1 0 1) doublet, suggesting that the sample was still amorphous.

In addition, the chemical environment of B and N atoms in the ceramic fiber was studied by XPS (Fig. 6). The B1s peak at 190.8 eV and the N1s at 397.7 eV confirmed the presence of BN [26], which is consistent with the XRD pattern. Moreover, the presence of B_2O_3 at 193.3 eV on the surface of the sample was also noticed, caused by high reactivity of B with respect to O [26]. Whereas the low peak of B_2O_3 indicated the incorporation

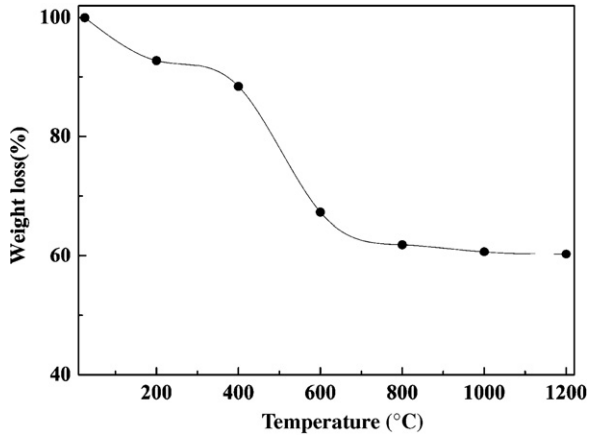


Fig. 3. TGA curve of cured fiber in NH_3.

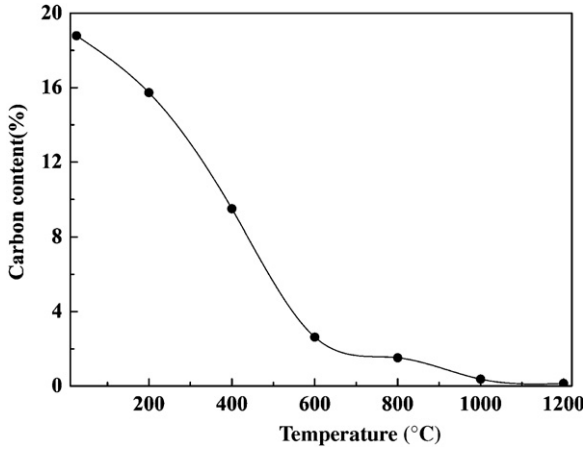


Fig. 4. Change in carbon content of cured fiber as a function of temperature.

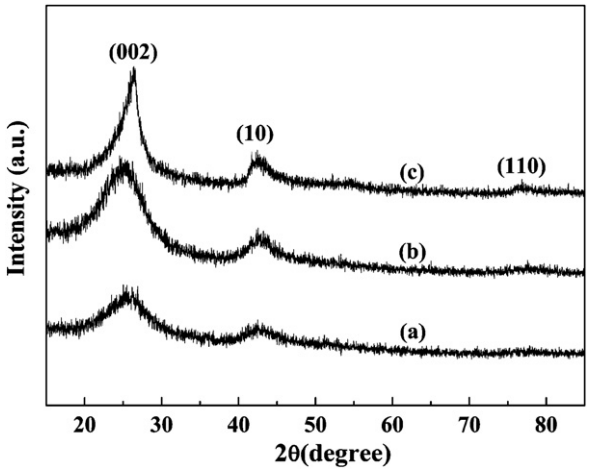


Fig. 5. XRD patterns of the BN fiber obtained at (a) 800 °C, (b) 1200 °C, and (c) 1400 °C.

of oxygen should be very weak, corresponding to the result of elemental analysis above.

Fig. 7(a) displays the typical morphology of the BN fiber, which exhibited a homogeneous surface morphology with a diameter of 13 μm. It is worth noting that the fiber shape was retained during curing and pyrolysis, suggesting that curing in NH_3 avoided inter-fiber fusion effectively. Moreover, some porosity could be noticed on the surface of fiber due to the release of carbon species and low molecular weight oligomers [7,27]. Due to these small defects, single tensile strength and Young's modulus of the fiber were determined as approximately 600 MPa and 30 GPa, respectively. Considering the dependence of fiber tensile strength on the diameter and crystallinity, great improvement could be achieved by increasing pyrolysis temperature, applying tension on fiber during pyrolysis process [28], etc. A detailed investigation of the BN fiber microstructure was investigated by high resolution transmission electron microscopy (HRTEM) with selected-area electron diffraction (SAED), as Fig. 7(b) and (c) shows, separately. Fig. 7(b) reveals a homogeneous phase for amorphous structure. The diffraction pattern [Fig. 7(c)] only illustrated a diffuse ring pattern of elastically scattered electrons, being characteristic for structures of short-range order [29]. Both were in good agreement with the XRD result above.

The materials for high temperature applications in oxygen-containing environments must embody excellent oxidation resistance [30]. Fig. 8 illustrates the TGA curve of as-prepared BN fiber and M-40 carbon fiber in air. For BN fiber, a little detectable weight loss happened before 400 °C, followed by a weight gain above 840 °C due to oxidation of BN to B_2O_3 [31]. As a comparison, M-40 carbon fiber began to oxidize at 500 °C and lost weight drastically above 600 °C owing to reaction of carbon and oxygen. The weight loss before 400 °C for BN fiber was due to vaporization of B_2O_3 formed on the original surface of BN at room temperature [32]. After processing at 800 °C for 4 h in air, the tensile strength and Young's modulus retention rate of BN fiber were about 70% and 61%. While M-40 carbon fiber has been oxidized completely and disappeared. As known, the oxidation behavior of BN was sensitive to its crystallinity

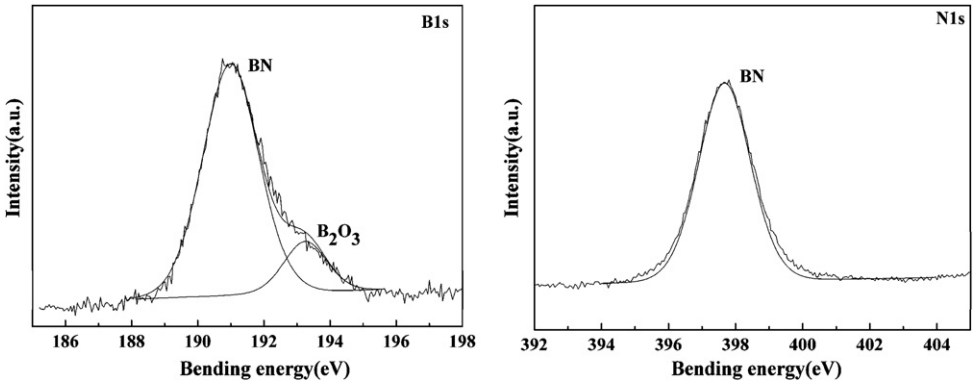


Fig. 6. XPS spectra of the BN fiber.

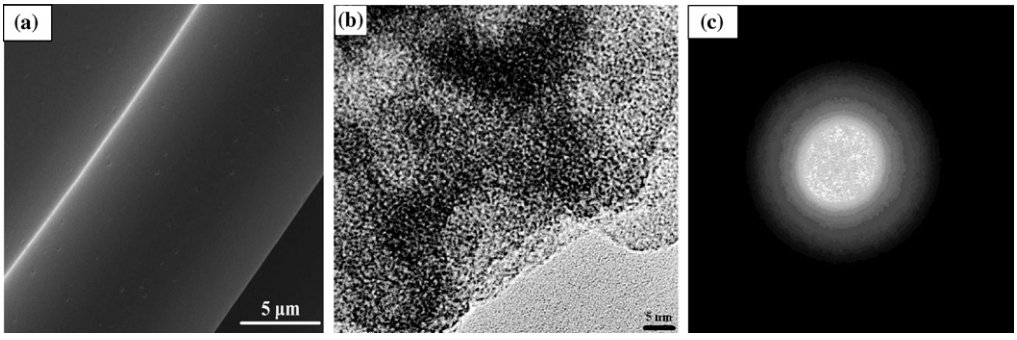


Fig. 7. SEM micrograph and HRTEM image of the BN fiber: (a) SEM micrograph, (b) HRTEM image, and (c) SAED pattern.

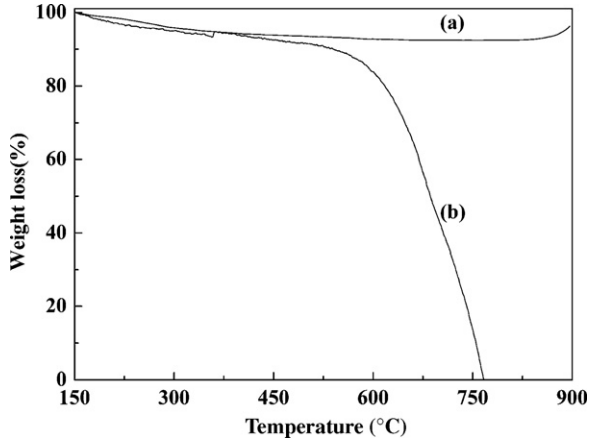


Fig. 8. TGA curves of (a) BN fiber and (b) M-40 carbon fiber in air.

and BN with higher crystallinity always possessed better oxidation resistance [33]. It is believed that the oxidation resistance of as-obtained BN fiber will be further increased by improving its crystallinity through elevating pyrolysis temperature.

4. Conclusions

In summary, a nearly stoichiometric BN fiber was prepared by curing and thermolysis of an easily synthesized poly[(alkylamino)borazine]. Curing in NH_3 rendered green fiber infusible and improved the ceramic yield evidently. Moreover, pyrolysis of the cured fiber in NH_3 led to a complete removal of carbon and exhibited a ceramic yield of 60 wt% at 1200 °C. The amorphous BN fiber with N/B molar ratio of 1.09 displayed a relatively low tensile strength of 600 MPa with an average diameter of 13 μm. Finally, the BN fiber presented good oxidation resistance in air. It is expected that properties of the BN fiber would be significantly improved by optimizing the thermolysis processes such as increasing pyrolysis temperature and applying tension on fiber during pyrolysis. The BN fiber developed in this paper is of interest for ceramic composites for applications in severe thermo-oxidizing environments.

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