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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

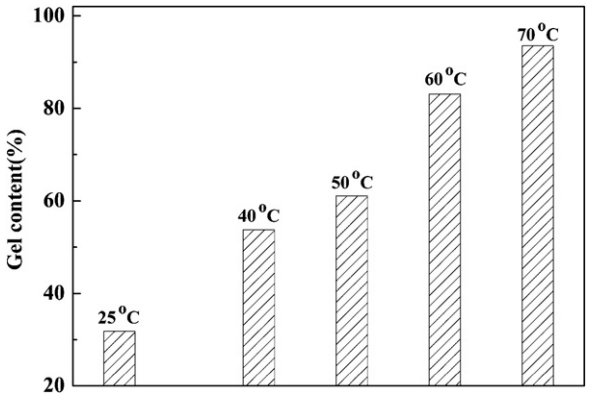


Fig. 1. Gel content of cured fiber obtained at different temperatures.

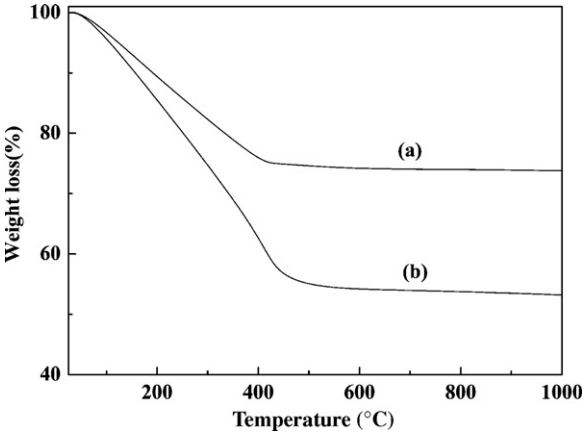
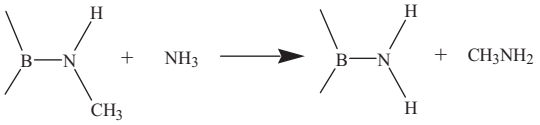
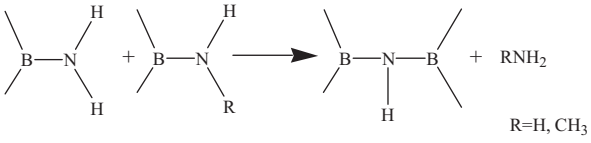


Fig. 2. TGA curves of (a) cured and (b) uncured fiber in Ar.

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.