

# Alkylaminoborazine-based precursors for the preparation of boron nitride fibers by the polymer-derived ceramics (PDCs) route

D. Cornu\*, S. Bernard, S. Duperrier, B. Toury, P. Miele

*Laboratoire des Multimatériaux et Interfaces, UMR 5615 CNRS, Bat. Berthollet, Université Claude Bernard, Lyon 1,  
43 Bd du 11 Novembre 1918, F-69622 Villeurbanne Cedex, France*

Available online 28 September 2004

## Abstract

Various borazine-based polymeric precursors can be prepared from tris(alkylamino)boranes and B-tri(chloro)borazine. Their chemical structures are described and compared in this review, along with their melt-spinnability. After polymer-to-ceramic conversion, the mechanical performances of the ensuing BN fibers are analyzed in relation with the structure of the corresponding thermoplastic polymers. The most promising results were obtained with B-tri(methylamino)borazine, which appears, at the present time, as the best candidate for a potential industrialization of the process. However, promising results were also obtained with borylborazines. This comparative study clearly emphasizes that the synthesis of tailored polyborazines is one of the key point for the preparation of high-performance BN fibers.

© 2004 Elsevier Ltd. All rights reserved.

*Keywords:* BN; Borazine; Boron nitride; Fibre; Preceramic polymer

## 1. Introduction

Boron nitride is an old commercial ceramic material of great importance for advanced technological applications. Similarly to carbon, different polymorphic forms of BN can be prepared, namely hexagonal (h-BN), cubic (c-BN), rhomboedral (r-BN) or würtzite (w-BN) boron nitride. The hexagonal polymorph is composed of sheets of hexagons, on the summits of which are alternatively placed boron and nitrogen atoms. All atoms are linked by covalent bonds within the sheets (*a*-axis) whereas two subsequent layers are linked by Van der Waals-type bonds (*c*-axis). The sheets are stacked up in such a way that hexagons of two consecutive layers are below each other and, along the *c*-axis, boron atoms alternate nitrogen atoms (Fig. 1). The anisotropic structure of h-BN provides unique mechanical, electrical, optical and thermal properties. The most relevant are the following:<sup>1</sup>

- Low coefficient of thermal extension (CTE), lower in *a* than in *c* direction

- Great resistance towards thermal shocks between 25 °C and 2000 °C (under nitrogen)
- Strong resistivity of  $3 \cdot 10^7 \Omega \text{ cm}$  in *a* direction and  $3 \cdot 10^9 \Omega \text{ cm}$  in *c* direction
- Great resistance towards oxidation upon 900 °C
- High tensile strength and Young's modulus in the *a* direction

As expected, these properties are highly dependent on the chemical purity, crystallinity and microstructural ordering of the samples and, thus, on their preparation method.

BN powders can be prepared by classical high-temperature route, involving cheap reagents like boric acid and urea (e.g.).<sup>2</sup> Most of the BN articles commercially available are made by hot-pressing of BN powders or by chemical vapor deposition (CVD) growth technique.

Among BN shaped materials, continuous thin fibers are of particular scientific and technologic importance, due to their potential application as fibrous reinforcements within composite materials, in replacement of carbon fibers for uses at high temperature in aggressive environment. Numerous works have been devoted to the preparation of BN fibers. Historically, Economy et al. were the first to achieve BN fibers in

\* Corresponding author. Tel.: +33 472 448 403.

E-mail address: [David.Cornu@univ-lyon1.fr](mailto:David.Cornu@univ-lyon1.fr) (D. Cornu).

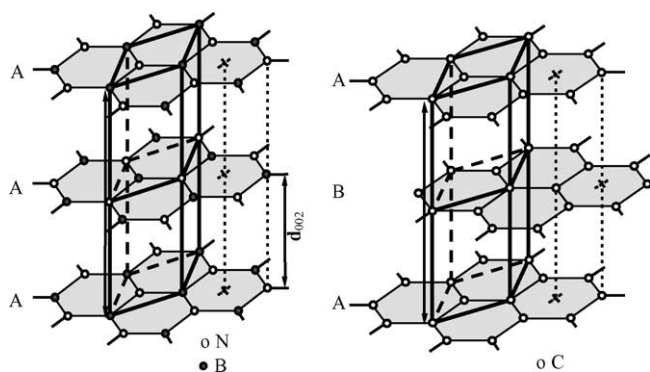


Fig. 1. Comparative crystallographic structure of h-BN and carbon graphite.

the 60s.<sup>3</sup> Their technique was based on the thermal nitridation of  $B_2O_3$  fibers by ammonia, followed by heat treatment at higher temperature under nitrogen. Although this technique allowed the fabrication of fibers with interesting mechanical properties (tensile strength,  $\sigma$ , of 1.3 GPa and Young's modulus,  $E$ , of 70 GPa), it presented some technological and purity inconveniences. First, control of the nitridation process was rather difficult and green fibers always contained residual oxide phases, which led to a decrease in their mechanical properties during ageing.

This conclusion clearly emphasized the need for a more versatile method for BN fibers preparation, namely the preceramic polymer route. The conversion of inorganic polymers into non-oxide ceramics was initially proposed by Lappert et al.<sup>4</sup> and Chantrell and Popper<sup>5</sup> in the 60s, and later developed by Yajima et al.<sup>6</sup> and Verbeek and co-workers<sup>7</sup> for the preparation of Si-based ceramic fibers in the 70s. This chemical approach was reviewed elsewhere.<sup>8</sup> It consists in the synthesis of a molecular precursor, its transformation into a preceramic polymer, which should be soluble and/or melt-processable, and finally the thermal and chemical conversion of the shaped crude product into ceramics like for instance ceramic fibers (Fig. 2).

Numerous studies were devoted to the synthesis of molecular and/or polymeric BN precursors in the past three decades. These works stimulated two reviews depicting 20 years of progress in the field of boron–nitrogen chemistry.<sup>1,9</sup> Among boron- and nitrogen-containing molecular compounds, borazine,  $H_3B_3N_3H_3$ , and its derivatives like the B-tri(alkylamino)borazines,  $[(RR')N]_3B_3N_3R''_3$ , are of particular interest (Fig. 3). Indeed, the borazinic core consists in a six-member ring, which is the basis of the structure of h-BN.

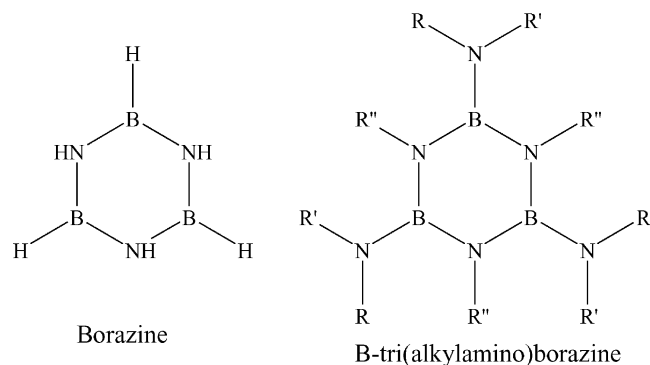


Fig. 3. Comparative structures of borazine and B-tri(alkylamino)borazine.

Two different strategies were investigated for the preparation of BN fibers. The borazinic ring may be either a part of the polymer backbone or be pendant to the polymer backbone. The latter was reviewed elsewhere<sup>9</sup> but, according to our knowledge, this kind of polymer has never been used for fiber preparation. It is interesting to notice that in addition to these two kinds of polymer, Seyferth and Rees produced BN fibers from linear polymers obtained by reaction of decaborane with diamines,  $[-B_{10}H_{12}\text{-diamine-}]_n$ .<sup>10</sup> Short green fibers were obtained from a dimethylformamide solution and their pyrolysis under ammonia up to 1000 °C gave BN fibers.

More suitable for large batch productions are the polymers derived from borazine,  $H_3B_3N_3H_3$ , namely the polyborazylenes. They were extensively studied in reason of their excellent ceramic yield, which is related to the absence of carbon-based groups in their structure. They were thermally synthesized via dehydrogenation reactions. The major encountered problem was that these polymers were thermoset and could not be melt-processed into shaped green articles, and particularly into polymer fibers. A possibility to overcome that drawback is to dissolve polyborazylenes into liquid borazine.<sup>11</sup> The resulting solution could exhibit a viscosity consistent with a spinning operation at 70 °C. The as-spun fibers were converted into BN fibers at 1250 °C under ammonia. Unfortunately, only few BN fibers of 3  $\mu\text{m}$  in diameter were prepared and they displayed many defects preventing their handling. An alternative route to overcome the thermoset behavior of polyborazylenes was proposed by Sneddon et al.<sup>12</sup> It consisted in the linkage of dipentylamino groups to the polyborazylene backbone, yielding the so-called “second-generation polyborazylene” polymers. Their rheological properties were appropriate for a melt-spinning step and flexible, uniform and defect-free crude fibers were prepared. A thermal treatment under ammonia up to 1000 °C led to the formation of amorphous BN fibers of  $\sim 30 \mu\text{m}$  in

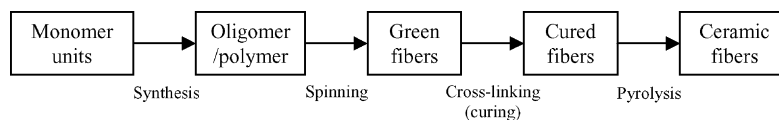


Fig. 2. General procedure for the preparation of ceramic fibers by the PDCs route.

Download English Version:

<https://daneshyari.com/en/article/9777940>

Download Persian Version:

<https://daneshyari.com/article/9777940>

[Daneshyari.com](https://daneshyari.com)