# Structural and Mechanical Behavior of Boron Nitride Fibers Derived from Poly[(Methylamino)Borazine] Precursors: Optimization of the **Curing and Pyrolysis Procedures**

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A series of boron nitride fibers were prepared by varying the tension applied on a same lot of poly(methylamino)borazine fibers during their pyrolytic conversion at 1800°C. Their microstructure/microtexture was studied by X-ray diffraction, scanning electron microscopy, and transmission electron microscopy investigations. Such analyses showed that ceramic fibers presented good crystallinity, but crystallites oriented along the fiber axis with fiber stress. It is most interesting that stretching was essentially effective during the pyrolysis to 1000°C, preventing fiber crimping, and decreasing the fiber diameter. Therefore, the fiber strength increased, while the fiber modulus also increased because of an improvement of the basal layer orientation along the *fiber* axis.

### I. Introduction

THE existence of ceramics has been known for a long time, **I** and they are fascinating materials, resulting in them being present in a wide range of domains ranging from day-to-day life utilization to specific high-tech applications. However, a common drawback of ceramics is their intrinsic brittleness, which limits their utilization, particularly as thermostructural materials. To overcome this problem, it was demonstrated that the fabrication of continuous fiber-reinforced ceramic composites (CFCCs) is the most effective alternative for development of nonbrittle ceramics.<sup>1-3</sup> "Graphitized" carbon fibers have been the most extensively studied reinforcing agent, resulting in numerous commercial developments of C/C composites.<sup>4</sup> Nevertheless, the low resistance of graphite toward oxidation  $(T_{\text{onset}} \approx 450^{\circ}\text{C})$  excludes the utilization of such fibers in a high temperature and a harsh environment. On looking at the main properties of several non-oxide ceramics one can notice that boron nitride (BN) could represent an interesting alternative to carbon for high-temperature structural applications owing to the isoelectronic character of the C-C and B-N bonds and the structural similarity of graphite and the hexagonal form of BN (*h*-BN), which is the most thermodynamically stable phase obtained under standard conditions.<sup>5,6</sup> Its lamellar structure is composed of basal layers (planes of hexagons), in which boron and nitrogen atoms alternate. Within the basal (002) layers (aaxis), the boron and nitrogen atoms are covalently bonded, whereas they are bonded through weak van der Waals interactions (c-axis) between subsequent stacked (002) layers. This structure results in unique properties, mostly anisotropic, which are of great interest for advanced technological applications. The most attractive properties are a high resistance to thermal

shocks up to 2000°C in an inert atmosphere, high mechanical properties along the (002) layers, an excellent chemical stability, and a very good resistance toward oxidation at a high temperature (upon ~900°–1000°C).<sup>7</sup> Above all, it exhibits a low coefficient of thermal expansion. Therefore, h-BN-based fibers (BN fibers) should be ideally suited for the reinforcement of ceramic matrix composites (CMCs) instead of carbon fibers in thermostructural applications, insofar as a method allows their preparation.

The fabrication of BN materials with complex shapes is difficult to achieve using conventional powder routes, particularly in the case of fibers. To prepare fibers, the pyrolysis of suitable molecular and polymeric precursors, usually referred to as the polymer-derived ceramics (PDCs) technique, appears to be the most appropriate.<sup>8-10</sup> This chemical approach is composed of several complex sequences summarized as follows: (1) design and synthesis of a molecular precursor, (2) its polymerization into a preceramic polymer composed of an inorganic backbone with pendent organic groups, (3) preparation of a covalent and amorphous ceramics at an intermediate temperature (with the aid of a chemical treatment if necessary), and (4) conversion into ultimate crystalline ceramics by a high-temperature thermal treatment. This route, in which a shaping step may be inserted between steps (2) and (3), was first developed for the fabrication of SiC and Si/C/N fibers.<sup>11–13</sup> Later it was extensively studied for other types of non-oxide ceramic fibers such as  $BN^{14-18}$  and SiBCN.<sup>19–21</sup>

Most spinnable polymers are based on the borazine molecule, which already foreshadows the hexagonal structure of *h*-BN and its B:N stoichiometry.<sup>22–25</sup> These studies showed that the presence of alkyl groups in the pendent borazine units and the type of linkages between the borazine rings in the polymer structure were prerequisites for preparing BN fibers. These general trends were confirmed in recent works published by our group.<sup>14–16,25–28</sup> In these studies, we showed that tri(alkylamino)borazines are excellent molecular precursors for developing polymers with controlled melt spinnability and thermal reactivity. Particularly, we have devoted a large part of our efforts toward poly[tri(methylamino)borazine] (polyMAB), because this polymer can exhibit a set of physicochemical properties of particular interest for the preparation of fine-diameter BN fibers with controllable mechanical and structural properties using spinning, curing, and pyrolysis procedures.<sup>16,25-26</sup> In previous works, we reported the chemical modifications, and the changes in the structural and mechanical features of fibers (crystallite sizes, crystallization degree, fiber strength, etc.) occurring during the polymer-to-ceramic conversion.<sup>16,26</sup> It was demonstrated that the curing of green fibers at 400°C in an ammonia atmosphere followed by the pyrolysis of as-cured fibers in ammonia (1000°C), then nitrogen (1800°C) atmospheres, yielded purely BN fibers with high mechanical properties.

In the present work, we focus our attention on the influence of some crucial parameters of the polymer-to-ceramic conversion on optimization of this conversion, and therefore controlling the mechanical properties of the final ceramic fibers. In

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particular, the present paper is devoted to both the study of the fiber stress that occurs during the pyrolytic conversion, and the effect of fiber tensioning on the mechanical and structural properties of BN fibers.

# **II. Experimental Procedure**

### (1) Characterization Techniques

All reactions were performed in an argon atmosphere and anhydrous conditions using a standard vacuum line, Schlenk techniques, and an efficient dry glove-box. The solvents were purified over appropriate drying agents by standard methods. The starting monomer, tri(methylamino)borazine (MAB), and the resulting polymer (polyMAB) were prepared following a procedure that has been described previously in the literature.<sup>16-17</sup> The differential scanning calorimetry analysis was performed on a ca. 15.0 mg sample using a TA8000 Mettler-Toledo apparatus (Viroflay, France) between  $-10^{\circ}$  and  $170^{\circ}$ C at a heating rate of 10°C/min in an argon atmosphere. The <sup>11</sup>B NMR spectrum was recorded on a Bruker AM300 spectrometer (Attlingen, Germany) at 96.28 MHz with  $Et_2O \cdot BF_3$  as an external reference (positive values downfield) in CH<sub>2</sub>Cl<sub>2</sub> solutions containing C<sub>6</sub>D<sub>6</sub> as an internal reference. <sup>1</sup>H and <sup>13</sup>C spectra were, respectively, obtained at 300 and 75 MHz in CD<sub>2</sub>Cl<sub>2</sub>. Size-exclusion chromatography analysis was performed in CH2Cl2 using a Gilson 118 UV detector (Villiers le Bel, France) at 240 nm and water styragel columns. Thermogravimetric analysis (TGA) was performed on a TGA 92 16-18 Setaram (Caluire, France) instrument at 1500°C (1000°C (ammonia atmosphere) + 1500°C (nitrogen atmosphere) at 0.8°C/min). Chemical compositions of the polymer were obtained from the Service Central de Microanalyses du C.N.R.S (Vernaison, France). X-ray diffraction (XRD) patterns were recorded between  $2\theta = 20^{\circ}$  and  $45^{\circ}$ using a Philips diffractometer (Almelo, the Netherlands) and CuK $\alpha_1$  radiation ( $\lambda = 0.1540$  nm at 40 kV and 30 mA) from asobtained fibers placed in a position so that the *fiber* axis is perpendicular to the incidence plane. The X-ray patterns obtained from the BN fibers exhibited some peak characteristics of h-BN by matching experimental patterns against reference patterns from the Joint Committee on Powder Diffraction Standards card data.<sup>29</sup> Intensities of the (hkl) peaks were given in relative units using the (002) peaks as a reference  $(I_{(002)} = 100\%)$ .<sup>27</sup> Transmission electronic microscopy (TEM) micrographs were obtained using a Topcon EMB-002B microscope (Yokohama, Japan) in both imaging and diffraction modes (diffraction patterns were obtained on 0.5 µm selected-area electron diffraction (SAED) patterns) on fragments of fibers embedded in an epoxy resin and then cut with an ultramicrotom (LEICA S, Vienna, Austria) as fully described in Chassagneux et al.28 The SAED mode was also used to estimate the local degree of orientation  $\omega_2$  of the basal layers along the *fiber* axis as described in Bernard et al.<sup>27</sup> Fibers were tensile tested at room temperature using an MTS-Adamel DY-22 tensile tester (Adamel Lhomargy, Roissy en Brie, France) equipped with a 5 N load cell, with the crosshead speed being 0.1 mm/min. The Weibull statistic was used to estimate the averaged tensile strength of fibers for a failure probability of 0.632 from a series of 50 fibers with a gauge length of 10 mm. The average Young's modulus was evaluated from the strain-strength curves.

# (2) Precursor Synthesis

114.7 g (683 mmol) of MAB was heated up to 200°C following a nine-step procedure: 1 h at 100°C, 1 h at 120°C, 2 h at 140°C, 20 h at 150°C, 7 h at 160°C, 17 h at 170°C, 24 h at 180°C, 5 h at 190°C, and 2 h at 200°C via major condensation of  $-N(H)CH_3$  units as illustrated in Scheme 1.

A vitreous yellow air- and moisture-sensitive solid, poly[(trimetylamino)borazine] (89.1 g) was obtained. Its molecular weight was  $M_w = 910$ ; and glass-transition temperature,  $T_g = 86^{\circ}$ C. The ceramic yield was  $\alpha = 53.9^{\circ}$ . Anal. found (wt%): C, 19.6; H, 7.9; B, 24.1; N, 48.4. Oxygen content was



**Scheme 1.** Schematic representation of the poly[tri(methylamino) borazine] (polyMAB) structure.

found to be lower than 2 wt%, and was therefore neglected. The other values were as follows: <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  (ppm): 30.7 (NCH<sub>3</sub> bridges), 27.68 (NHCH<sub>3</sub>);. <sup>11</sup>B NMR  $\delta$  (ppm): 25.96 (br); <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  (ppm): 1.89 br (NHCH<sub>3</sub>), 3.39 br (NH borazine), 2.58 vbr (NHCH<sub>3</sub>, NCH<sub>3</sub>); and FT-IR/KBr (cm<sup>-1</sup>): 3447 (v<sub>N-H</sub>), 2948, 2894 (v<sub>C-H</sub>), 1478 ( $\delta_{N(H)CH_3} + v_{B-N} + \delta_{asCH_3}$ ), 1161 (v<sub>C-N</sub>), and 609 ( $\delta_{BN}$ , out-of-plane).

## (3) Fiber Preparation

Poly(methylamino)borazine fibers (green fibers) were obtained using the general melt-spinning process (nitrogen atmosphere) described previously<sup>26</sup> from a same lot of polymer. In particular, the polymer was spun at 180°C, and emerged as an endless green fiber from the spinneret with a capillary of 200  $\mu$ m diameter. The as-spun fiber was immediately stretched into a finer-diameter green fiber by a winding graphite spool that exhibited a negligible coefficient of thermal expansion (Carbone Lorraine, Paris, France). The polyMAB fiber emerged as continuous green fibers wound on the spool.

After the melt-spinning operation, a series of three bundles of the green fiber, labeled **A**, with an initial equivalent length (15.70 cm) and diameter (14.9  $\mu$ m), was isolated to undergo pyrolytic conversion (in an ammonia atmosphere up to 1000°C (0.8°C/ min, atmospheric pressure), and then in a nitrogen atmosphere up to 1800°C (0.8°C/min, atmospheric pressure)) as follows:

(1) The first bundle of **A** was cut along the spool after the melt spinning, which resulted in a lack of any tension during the subsequent pyrolytic conversion into BN fibers **A-1**.

(2) The second bundle of **A** was maintained around the spool to undergo curing ( $400^{\circ}$ C; ammonia atmosphere) and mineralization ( $1000^{\circ}$ C; ammonia atmosphere) steps under tension. After such heat treatments at  $1000^{\circ}$ C, as-mineralized fibers were cut along the spool to be transformed without tension into BN fibers **A-2** between  $1000^{\circ}$  and  $1800^{\circ}$ C in a nitrogen atmosphere.

(3) A third bundle of **A** was maintained around the spool during the whole classical pyrolytic conversion at 1800°C into BN fibers **A-3**. It is therefore considered to be under tension during the whole pyrolytic conversion.

## III. Results

# (1) Scanning Electron Microscope (SEM) Observations

The green fibers A, 15.70 cm in length and 14.9  $\mu$ m in diameter, were prepared in the same batch, and thus pyrolyzed together up to 1800°C with different applied tensions as mentioned in the experimental procedure. Figure 1 shows the SEM image of a typical green fiber A after a melt-spinning operation. Its featureless cross-sectional microtexture is similar to that of common organic polymer fibers. Defects appeared neither in the volume nor on the fiber surface.

The green fiber was cured in an ammonia atmosphere (400°C), and then pyrolyzed in ammonia (1000°C) and nitrogen (1800°C) atmospheres yielding BN fibers A-1 (without applied tension), A-2 (green fiber maintained under tension up to  $1000^{\circ}$ C), and A-3 (green fiber maintained under tension up to



Fig. 1. Scanning electrom microscope image of the cross-sectional microtexture of the green fiber A.

1800°C). After the pyrolytic conversion, as-obtained ceramic fibers were white in color and of flexible form, but it was observed that fibers **A-1** were considerably crimped. Nevertheless, despite the different morphologies, no significant microtex-

tural differences were observed from SEM investigations as illustrated in Fig. 2.

In particular, the three types of fibers displayed a circular cross section similar to that of the original green fiber A, which means that the polymer possessed a reactivity tailored for the curing and pyrolysis procedures, and is thus ideal for generating materials without loss in fiber integrity. Fibers were smooth and free of surface defects, and their cross-sectional microtexture did not exhibit marked differences. Observations of these cross-sections revealed a similar grainy microtexture as opposed to the featureless cross-sectional microtexture of the green fiber (Fig. 1). This coarse-grained microtexture is characteristic of sintered crystalline ceramic materials. Furthermore, considering the findings in SEM and laser interferometry investigations (Table I), the fiber diameter decreased in the sequence A-1 (10.7  $\mu$ m,  $\Delta \phi / \phi_0 = 28\%$ ) > A-2 (9.4  $\mu$ m,  $\Delta \phi / \phi_0 = 37\%$ ) > A-3 (8.4 µm,  $\Delta \phi / \phi_0 = 43.6\%$ ). Besides, the original length of the green fiber A (l = 15.70 cm) was not retained in the resulting BN fibers A-1 ( $l \sim 12$  cm), and A-2  $(l \sim 14.6 \text{ cm})$ . In contrast, it was slightly increased in BN fibers A-3  $(l \sim 16.20 \text{ cm})$ .

The observed differences in the measured values of diameters and lengths could be easily correlated to the shrinkage that the green fiber  $\mathbf{A}$  underwent during its pyrolytic conversion.

As the same green fiber was used as precursor for BN fibers, and the same temperature and heating rate conditions were applied, Table I shows that the tensile strength of BN fibers is indirectly related to the fiber stress, as it was shown that the strength of fibers A-1 was about 20% lower than those of BN fibers A-2 and A-3. The strengths of fibers A-2 and A-3 are similar, and as-obtained strengths for such fibers heated under



Fig. 2. Scanning electron microscope images of the cross-sectional microtexture of boron nitride fibers A-1, A-2, and A-3.

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| Table 1. Flivsical Fluperties of the Three Types of Div Fluer | Table I. | Physical | <b>Properties</b> | of the | Three | Types | of BN Fiber |
|---|----------|----------|-------------------|--------|-------|-------|-------------|
|---|----------|----------|-------------------|--------|-------|-------|-------------|

| Fiber type | Diameter (µm) | Strength $\sigma$ (GPa) | Modulus E (GPa) | Strain $\epsilon$ (%) | $L_{\rm c}$ (nm) | $L_{\rm a}$ (nm) | <i>d</i> <sub>002</sub> (nm) | ω    | ω <sub>2</sub> |
|------------|---------------|-------------------------|-----------------|-----------------------|------------------|------------------|------------------------------|------|----------------|
| A-1        | 10.7          | 0.9                     | 110             | 0.72                  | 9.9              | 21.3             | 0.339                        | 0.37 | 0.3            |
| A-2        | 9.4           | 1.1                     | 285             | 0.36                  | 9.0              | 21.9             | 0.336                        | 0.85 | 0.9            |
| A-3        | 8.4           | 1.2                     | 285             | 0.44                  | 8.6              | 18.2             | 0.337                        | 0.85 | 0.9            |

BN, boron nitride.

tension were typically those found for high-performance BN fibers studied in previous papers.<sup>26,27</sup>

# (2) XRD Investigations

The XRD patterns of the three types of as-obtained BN fibers were nearly identical (in terms of definition and broadening of the peaks), and revealed a polycrystalline nature (Fig. 3), despite a slight shift of the (002) peaks to higher Bragg's angles from **A-1** ( $2\theta_{(002)} = 26.27^{\circ}$ ) to **A-3** ( $2\theta_{(002)} = 26.43^{\circ}$ ), approaching closer to the  $2\theta_{(002)}$  position found in *h*-BN crystals ( $2\theta_{(002)} = 26.76^{\circ}$ ).

As an illustration, XRD data are reported in Table I. Table I shows that significant differences were found neither in the average crystallite sizes nor in interlayer spacing. However, although the crystallite sizes are similar, irrespective of the kind of ceramic fibers, their orientation along the *fiber* axis differs significantly. This characteristic is immediately clear in XRD patterns reported in Fig. 3. We recently reported that an average degree of orientation  $\omega_1$  of the (002) layers along the fiber axis could be estimated by comparing the intensity ratio of the above-mentioned diffraction peaks in both XRD patterns obtained from as-pyrolyzed fibers (Fig. 3) and those after grinding (groundup samples, not shown in the present paper).<sup>27</sup> Accordingly, the higher the  $I_{(002)}/I_{(10)}$  ratio in as-obtained BN fibers (Fig. 3), the higher the average orientation degree  $\omega_1$ . This ratio theoretically increases from 0 for polycrystalline h-BN without orientation effects of grains to 1 for perfectly oriented BN grains. For fibers A-2 and A-3,  $\omega_1$  is around 0.85 (high  $I_{(002)}$ /  $I_{(10)}$  ratio, Fig. 3), which suggests the same degree of orientation of the (002) planes compared with the *fiber* axis, whereas fibers **A-1** display a poor orientation level (low  $I_{(002)}/I_{(10)}$  ratio, Fig. 3). According to the modulus data given in Table I, the increased orientation of the basal (002) layers from A-1 to A-3 is clearly accompanied by a significant increase in the fiber modulus of the corresponding fibers, as generally observed in BN fibers.<sup>2</sup> ' As the modulus E emerged stronger than the fiber strength  $\sigma$  with the applied fiber stress, it was observed that the failure strain  $\varepsilon$  $(\varepsilon = \sigma/E)$  significantly decreased with the applied fiber stress.

# (3) TEM Studies

In order to confirm the structural/textural/mechanical properties' relationship, the microstructure and the texture of BN fibers were investigated by TEM. For example, a bright-field (BF) micrograph of a longitudinal thin section of fibers A-3, in which the corresponding SAED pattern is inserted, is shown in Fig. 4. Consistent with SEM analysis, the BF TEM image of A-3 represents a coarse-grained microtexture indicating a well-ordered and crystallized material. Data provided by SAED of such fibers reflected the XRD results considerably. In particular, the SAED pattern displayed rings of (002), (10), (004), (110), and (112) planes of *h*-BN.<sup>29</sup> Moreover, the diffracted (001) rings were discontinuous as arcs, which demonstrated a preferred orientation of these planes compared with the *fiber* axis.<sup>§</sup>

The estimation of the alignment of (002) layers in a direction parallel to the *fiber* axis, as quoted above from the XRD data, was also possible from SAED patterns by calculating the degree of orientation  $\omega_2$ . In fibers A-3, it was found to be around 0.9, in the same order of magnitude as that obtained from XRD

patterns ( $\omega_1$ ). Both values are close to that reported by Okano and Yamashita<sup>30</sup> in a patent describing the fabrication of highperformance BN fibers with highly oriented crystallites. The comparison between (002) dark-field (DF) mode and the BF normal mode (Fig. 5) obtained at higher magnification of the same part of the fibers allows positive identification of the regions in the specimen that contributed to a particular reflection, i.e., (002) reflection, in the diffraction pattern. By selecting only the (002) beam to form the DF image, the regions of the fiber having scattered, this beam appeared bright on a dark background, so that the image is formed only from those crystallites diffracting electrons into the (002) beam. Each bright domain images a single crystallite (circled in Fig. 5), and the extent of the network is that of a local crystallite orientation. The dark areas in the DF image correspond to other crystallite orientations, either twisted or tilted considerably to allow their (002) beams to pass through the aperture.

The presence of some rhombohedral BN crystals generally found in the close vicinity of internal pores in high-resolution TEM (HRTEM) images (Fig. 6), as it was recently described, is also remarkable.<sup>28</sup> Nevertheless, HRTEM investigations of such fibers frequently show local hexagonal segregation embedded in a turbostratic BN phase. The turbostratic BN phase (*t*-BN) has already been described elsewhere.<sup>31</sup>

A similar analysis was performed on fibers **A-2** and the same conclusions concerning the orientation of the (002) layers were drawn. For example, Fig. 7 shows the BF TEM image of a longitudinal section of such fibers, which is similar to that of the BN fibers **A-3**.

The associated SAED pattern could consistently be indexed as previously. SAED of fibers A-2 is also representative of an ordered material. A good orientation can immediately be observed in the low spread of the (002) spot ( $\omega_2 \sim 0.9$ ). Similarly, the orientation of the (002) planes was consistent with the perfect superimposition of the BF and (002) DF images (not shown in the present paper) taken at a higher magnification.

The BN fiber A-1 was analyzed in the same manner. Figure 8 shows the BF TEM micrograph in which the crystal growth is clear as observed previously. This observation reflected XRD data and highlighted the similarity in the crystallinity level between the three types of BN fibers.



Fig. 3. X-ray diffraction patterns of as-obtained boron nitride (BN) fibers, from A-1 to A-3.

<sup>&</sup>lt;sup>§</sup>In the case of randomly oriented planes of hexagons, the diffraction spot would be a circle of regular intensity and an infinitely small point for a perfectly oriented crystal. It should also be noted that there is a shift of angle between the image mode and the diffraction mode, resulting in apparent different directions between the image and the diffraction pattern.



**Fig. 4.** Bright-field transmission electron microscope image and the associated selected-area electron diffraction of the longitudinal sectional microstructure of boron nitride fibers **A-3**.

In contrast, some differences appeared in the associated SAED pattern. Although the microstructural ordering of such fibers seems to be similar to those of fibers A-3 and A-2, the SAED pattern is composed of almost (002) circles, demonstrating that the (002) layers are randomly distributed compared with the *fiber* axis. The low calculated degree of orientation  $\omega_2 \sim 0.3$  confirmed such observations.

# IV. Discussion

Previous results demonstrated that the control of the green fiber stress that occurs during the whole pyrolytic conversion is an important requirement to maintain the original fiber morphology and improve the mechanical properties of BN fibers. As previously reported by our group, it was demonstrated that room temperature strength and toughness were correlated to the



Fig. 6. High-resolution transmission electron microscopy micrographs of the longitudinal sectional microstructure in boron nitride fibers A-3.

microstructural and microtextural state of the BN single phase. In particular, the fibers must undoubtedly report a high level of crystallinity and microstructural ordering of the hexagonal polymorph, while the average preferred orientation of the layers of hexagons (002 planes) also appears to be of particular importance.<sup>26</sup> Indeed, with the BN fibers investigated in the present paper, quite independent of their origin, a well-established correlation exists between the preferred orientation of the (002) layers and Young's modulus: the more highly oriented the (002) layers, the higher the fiber modulus.

# (1) Shrinking Effects

The use of tension during the heat treatment of green fibers was investigated as a possible means of increasing the mechanical properties of final BN fibers.

BN fibers A-1, A-2, and A-3 were prepared from the same batch of polymer using the same spinning parameters, and with identical curing and pyrolysis procedure conditions (temperature, heating rate, and atmosphere). In order to evaluate the role of the tension applied on the green fiber A because of the com-



Fig. 5. Imaging of the preferred orientation of (002) planes along the *fiber* axis.



**Fig. 7.** Bright-field transmission electron microscope image and the associated selected-area electron diffraction of the longitudinal sectional microstructure of boron nitride fibers **A-2**.

bination of the shrinking effects of the material and the use of a spool during the pyrolytic conversion, two types of fibers were cut at different stages of the transformation: (1) before the pyrolytic conversion leading to BN fibers A-1 and (2) after the thermal treatment in an ammonia atmosphere at 1000°C providing BN fibers A-2. In contrast, BN fibers A-3 were produced through the classical pyrolytic conversion of the preceramic green fiber A wound on the spool.

The first consequence of these changes in tension was the increased diameter of ceramic fibers, and the concomitant decreased length when the global longitudinal fiber stress decreased. In particular, the green fiber A significantly shrank in length owing to the large two-step weight loss  $(\Delta m/m_0 = 43.9\%)$  and the density increase  $(\Delta d/d_0 = \sim 30\%^{26})$  that occurred during the pyrolytic conversion up to  $1000^{\circ}$ C in an ammonia atmosphere. Upon heat treatment in a nitrogen atmosphere in the temperature range  $1000^{\circ}$ -1800°C, minor changes in fiber lengths were observed, as the total ceramic yield was 53.9%, while a fiber density of 1.9 was generally obtained.<sup>26</sup>



**Fig. 8.** Bright-field transmission electron microscope image and the associated selected-area electron diffraction of the longitudinal sectional microstructure of boron nitride fibers **A-1**.

The sintering mechanism by which green fibers provided ceramic fibers could be explained based on the mass changes and density increase data. The shrinkage, which occurred during the curing and pyrolysis procedures of the green fibers **A** into ceramic fibers **A-(1-3)** inducing loss of gaseous byproducts (methylamine and ammonia<sup>16</sup>), occurred according to the following equation:

$$\mathbf{A}_{s} \rightarrow \mathbf{A} - (\mathbf{1} - \mathbf{3})_{s} + \text{gaseous by products}$$
 (1)

The fiber shrinkage depends on changes in material mass and density increase. In this context, taking into account the circular cross-sectional morphology of fibers, the relative change in volume ( $\Delta V$ ) could be expressed in terms of the ceramic yield ( $\alpha$ ) and the density (d) as follows:

$$\Delta V(\%) = \frac{100m_0(d_{\rm c} - d_{\rm p})}{d_{\rm p}d_{\rm c}V_{\rm p}} = \frac{100(d_{\rm c} - \alpha d_{\rm p})}{d_{\rm c}}$$
(2)

with  $d_c$  and  $d_p$  being the density of the ceramic fibers ( $d_c = 1.9^{26}$ ) and that of green fibers ( $d_p = 1.2$ ), respectively.  $m_0$  is the initial mass of the polymer, and  $V_p$  and  $V_c$  are the polymer and ceramic volumes, respectively.

According to the value of the final mass loss ( $\Delta m/$  $m_0 = 46.1\%$ ,  $\alpha = 53.9\%$ ) after the curing and pyrolysis procedures of the green fiber to form BN fibers, a shrinkage in volume by 66% was estimated. Considering this estimated value, it is shown that the empirical volume loss associated with the A-to-A-1 conversion is only  $\sim 58\%$ . This lower value suggests that the amount of stress to which the green fiber was subjected during the pyrolytic conversion also affected the fiber density. It can be estimated at 1.65 in the present case. It is therefore probable that the fiber stress causes the internal pores (owing to the spinning and pyrolytic conversion procedures) to collapse. Therefore, the considerable reduction in length during the transformation of the green fiber A into ceramic fibers A-1 occurred to the detriment of that of diameter, and yielded crimped BN fibers. In contrast, fibers A-2 and A-3 were maintained around the spool either during a part (1000°C, fibers A-2) or the whole (1800°C, fibers A-3) pyrolytic conversion, so that the longitudinal shrinkage was significantly reduced, especially in the case of fibers A-3. The latter were even slightly slackened around the spool, resulting in an increased length. Such phenomena could be related to the slight unwinding of the lubricating continuous BN fiber around the spool at high temperature. Therefore, the fiber crimping was limited, and most of the volume change was associated with diameter loss. It was interesting to note that the longitudinal shrinkage occurred in an ammonia atmosphere up to 1000°C as well as in a nitrogen atmosphere from 1000° to 1800°C. The concomitant decrease in the practical strengths with increased diameters showed that tension was an essential requirement for enhancing the strength of BN fibers.

# (2) Effect of Tension on the Fiber Properties

SEM and XRD of the three fibers (see Fig. 2) reflected a good level in the crystallinity and microstructural ordering. The patterns displayed most of the peaks corresponding to h-BN, despite collecting the (100) and (101) reflections in a single broad (10) peak, which is characteristic of a two-dimensional ordering as a turbostratic boron nitride (t-BN).<sup>31</sup> Consequently, the phases displayed only a partial three-dimensional order as a mesohexagonal BN phase.<sup>27</sup> The comparatively high crystallinity was reflected in the generally sharp full-width at half-maximum of the diffraction peaks, an effect usually thought to be because of a high crystallite size as calculated. The values were in the order of 9 and 20 nm for  $L_c$  and  $L_a$ , respectively, which showed that the BN fibers were relatively well-ordered, from a structural point of view, and that the grain growth seemed to be independent of the fiber stress during the pyrolytic conversion. In particular, it is interesting to note that the crystallite stack height

and length do not increase for crystallites oriented at an increased angle to the *fiber* axis.

XRD and TEM data highlighted the correlation between the fiber modulus and the microstructural and microtextural properties. In particular, the present paper shows that the Young's modulus of BN fibers was closely related to the orientation of the basal (002) sheets along the *fiber* axis. It was observed that the fiber stress appears to be one procedure that may yield considerably increased fiber modulus. This trend has been clearly established in the case of carbon fibers,<sup>32</sup> and could be logically expected for BN fibers considering their structural similarity and the high in-plane average B–N bond energy  $(D(B-N) \sim 500.75)$ kJ/mol<sup>33</sup>). The Young's modulus was significantly lower for BN fibers A-1 than those determined for fibers A-2 and A-3, in accordance with the values found in the orientation degrees  $\omega_1$  and  $\omega_2$ . However, considering the identical values in modulus and orientation degree for fibers A-2 and A-3, it was surprising to note that the first step of the pyrolysis occurring in an ammonia atmosphere up to 1000°C under tension of the green fiber A was an important requirement for increasing such values. These observations can be related to those in carbon fibers, which showed that the application of tension during curing is important to prevent polymer chains from relaxing and losing their orientation.<sup>34</sup> In contrast, the applied tensioning was observed to be essentially ineffective during the heat-treatment region from 1000° to 1800°C, and in particular, during the crystallization process  $(1400^{\circ}-1800^{\circ}C^{26})$ , despite the importance of fiber stress as discussed above. Such results are in contradiction with those of carbon fibers for which a tensioning at high temperature should be maintained to improve the mechanical properties of fibers.<sup>34</sup> However, it should be mentioned that carbon fibers are derived from polyacrilonitrile, which displays a noncomparable higher molecular weight than the poly[(methylamino)borazine]. Nevertheless, the reason for this ineffectiveness at very high temperature has not yet been understood, but it can be viewed that a higher mechanical tension should be applied during the ceramic stage to improve orientation.

It is established that a preorientation of the growing molecular borazine ring units, to some degree associated with the fiber stress, occurs during the cross-linking and mineralization steps of the green fiber in an ammonia atmosphere up to 1000°C. For this reason, BN fibers with an increased degree of preferred orientation, and hence improved fiber mechanical properties are obtained. Furthermore, it was also observed that the preferred molecular orientation was maintained even without tension in the temperature range 1000°-1800°C, despite numerous structural rearrangements.

### V. Conclusion

The optimization of the curing and pyrolysis procedures for the preparation of BN fibers from a melt-spinnable poly[(methylamino)borazine] was reported. The study was focused on the effect of the shrinking effects and fiber stress on the mechanical and structural behavior of the resulting BN fibers.

The crystallinity and microstructural ordering of three types of BN fibers A-1, A-2, and A-3 obtained from a same lot of green fiber A were similar irrespective of the tension applied during the pyrolytic conversion. In particular, both XRD and TEM analyses were representative of BN materials ordered in a meso-hexagonal stacking sequence. However, differences in the textural orientation of the fibers were highlighted by XRD analysis and TEM investigations. For example, a pronounced orientation of the basal (002) planes along the *fiber* axis was shown in fibers A-2 and A-3, for which tension was applied during a part (1000°C, fibers A-2) and the whole (1800°C, fibers A-3) pyrolytic conversion. In contrast, no orientation effects of the BN crystallites were observed in fibers A-1, which were not maintained around the spool during ceramic conversion. In the latter, the fiber crimping was clearly pronounced according to the reduction in both their length and diameter. In particular, it was shown that tensioning was already effective below 1000°C, improving the degree of orientation of the basal layers along the fiber axis, and therefore, the modulus in the final BN fibers. In addition, tensioning was also effective in decreasing the fiber diameter, and therefore increasing the strength of the resulting final BN fibers produced at 1800°C. Further studies are in progress to quantify and optimize (1) the stress that has to be applied on green fibers in order to prevent fiber breakage and (2) the restricted temperature range within which the fibers must be stressed.

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