Section 6. Polymers

Chemical tailoring of *Single-Source* molecular and polymeric precursors for the preparation of ceramic fibers

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The present paper reports the preparation of non-oxide ceramic fibers through the Polymer-Derived Ceramics (PDCs) route. The poly[*B*-(methylamino)borazine]-derived boron nitride (BN) ceramic fibers and modified C-B-C-bridged polysilazanes-derived silicoboron carbonitride (SiBCN) ceramic fibers were used as models. The chemical tailoring of BN or SIBCN molecular and polymeric precursors, achieved by the introduction of plasticizing pendent groups such as Si-CH$_3$ and NCH$_3$/N(H)CH$_3$ in the structure, has been shown to improve the melt-spinnability of preceramic polymers. Such pendent groups allowed of controlling both melt-viscoelastic properties and thermal reactivity, and then to produce high quality fine-diameter endless green fibers via a stable melt-spinning process. Fibers were subsequently cured through a chemical process using ammonia as curing agent. As-cured fibers were then pyrolyzed in a controlled atmosphere depending on the desired ceramics. BN fibers were prepared by pyrolysis in an ammonia atmosphere at 1000 °C to remove the carbon elements from the materials, then in a nitrogen atmosphere at 1800 °C to microstructurally design the boron nitride phase and produce polycrystalline ceramic fibers. SiBCN fibers were obtained through pyrolysis of as-cured fibers at 1400 °C in a nitrogen atmosphere. Ceramic fibers are delivered in a controlled chemical composition with form retention.

1. Introduction

The Polymer-Derived Ceramics (PDC) approach is a non-conventional chemical route in which *single-source* precursors containing all the elements desired in the final ceramics are used as starting compounds [1,2]. Transitional stages in this process consist in the preparation of preceramic polymers[1] from molecular precursors followed by an optional shaping process of these preceramic compounds, and the conversion of materials into nanostructured ceramics with retention of the desired form.

The chemical tailoring of molecular and polymeric precursors is a fundamental requirement for the preparation of refractory ceramic fibers with desirable structural and mechanical properties [3-6]. Among others, through the control of polymer composition and architecture, spinnability and thermal reactivity of polymers can be controlled at low temperature to generate after pyrolytic conversion amorphous or polycrystalline ceramic fibers depending on the desired properties.

Polycristalline ceramic fibers are seen as reinforcing agents for materials in various types of applications in which specific properties (thermal conductivity, electrical insulation, and chemical inertia) are required. In contrast, amorphous ceramic fibers as metastable solid solutions are especially destined to ultra-high temperature applications where a durability of the amorphous microstructure and the mechanical properties is a crucial requirement.

The present paper reviews the recent efforts we have made in the field of the preparation of polycrystalline BN (boron nitride) fibers and amorphous SiBCN (silicoboron carbonitride) fibers and demonstrates through these two models how the chemical tailoring of molecular and polymeric precursors is an useful pathway to provide high-performance ceramic fibers.

2. Experimental

2.1. General Comment

All synthesis reactions were carried out in a purified argon atmosphere using standard Schlenck and vacuum-line techniques. Solvents were distilled over appropriate drying reagents.

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[1] We will use in the present paper the term « polymer » in its broadest sense, that is, as a group of molecules whose structure can be generated through repetition of one or a few elementary units.

2.2. Poly[*B*-(methylamino)borazines] preparation

Glassy and colorless poly[*B*-(methylamino)borazine] was synthesized in a three-necked reactor by thermolysis of 70g (419 mmol) of *B*-(methylamino)borazines up to 185 °C under vigorous stirring.

2.3. Preparation of C-B-C-bridged polysilazanes containing N-CH₃ units

In a 2 l Schlenk flask equipped with a water-cooled reflux condenser, a gas inlet tube and a magnetic stirrer, trisdichlorosilylethylboranes $B(C_2H_4SiRCl_2)_3$ (30.80 g (70.9 mmol), R=CH₃; 26.56 g (67.24 mmol), R=H) were dissolved in 500 ml of toluene and cooled to 0°C. Under vigorous stirring, a large excess of methylamine (19.82 g (638.1 mmol), R=CH₃; 18.80 g (605.2 mmol), R=H) was introduced through the solution which immediately caused the precipitation of methylamine hydrochloride. After the addition of methylamine was completed, the reaction mixture was allowed to warm to room temperature and the polymer solution was filtered through a pad of Celite. The filtrate and the extract were combined, concentrated and dried in a high vacuum (10^{-2} mbar) to produce polymers of the type $[B(C_2H_4SiRNCH_3)_3]_n$ (20.90 g (66.50 mmol, 96%), R=CH₃; 15.63 g (58.02 mmol, 86 %), R=H).

2.4. Fiber preparation

Green fibers were prepared in a nitrogen atmosphere using a lab-scale melt-spinning apparatus set up in a glove-box. Polymers were melt-spun through a spinneret having a single 0.2 µm capillary and the resulting endless filaments were subsequently stretched and collected on a rotating spool. As-spun fibers were cured in an ammonia atmosphere up to 200 °C (SiBCN fibers) and 400 °C (BN fibers) in a silicate tube furnace. The heat treatment was followed by pyrolysis in a nitrogen atmosphere up to 1400 °C for the preparation of SiBCN fibers, whereas it was achieved in an ammonia atmosphere up to 1000 °C, and then in a nitrogen atmosphere up to 1800 °C for preparing BN fibers. Fibers were maintained around the spool during the whole conversion to prevent crimping and loss of fiber integrity.

2.5. Characterization techniques

Chemical analysis was performed using a combination of different analysis apparatus (ELEMENTAR Vario EL CHN-Determinator, ELTRA CS 800 C/S Determinator, LECO TC-436 N/O Determinator) and by atom emission spectrometry (ISA JOBIN YVON JY70 Plus).

Differential scanning calorimetry (DSC, Mettler Toledo DSC TA 8000) was conducted in a nitrogen atmosphere (20-200 °C; heating rate: 10 °C.min⁻¹) in aluminum crucibles. Thermo-mechanical analysis (TMA, Mettler Toledo TMA/SDTA 840) was carried out in a nitrogen atmosphere (30-140 °C; heating rate: 5 °C.min⁻¹).

The pyrolytic yield are obtained by heating samples at 0.8 °C.min⁻¹ from 20 °C to 1000 °C in flowing ammonia and nitrogen (TGA 92 16.18 by SETARAM).

Fiber morphology was observed by scanning electron microscopy (SEM) with field emission equipment, Hitachi S800.

Average molecular weight values were determined by Size Exclusion Chromatography (SEC). Analyses were performed using a Shimadzu SPD 6A UV detector and Waters s-Styragel Columns with THF as eluent.

Shear rheology measurements were carried out at the National Center for Engineering Systems with Complex Fluids (NCESCF, Timisoara, Romania) on a Paar Physica MCR 300 oscillatory rheometer placed in glove-box filled with argon (Linde Gas). Frequency-sweep tests were performed in the linear viscoelastic range, using controlled strain amplitude (γ=0.1) and plate and plate geometry (25 mm in diameter) with a 0.5 mm gap.

3. Results and discussion

3.1. Polymer synthesis

The design strategy for preparing spinnable polymers is based on the chemical functionalization of molecular precursors and/or preceramic polymers with pendent groups of appropriate chemical composition and controlled cross-linking properties without affecting the final quality of ceramics. Two routes are generally explored for the incorporation of specific pendent groups in the precursor structure. They are reported in the present chapter through examples dedicated to BN and SiBCN precursors.

3.1.1. Modified borazine-based polymers – The poly[B-(methylamino)borazines]

The borazine molecule (Fig. 1) represents the best precursor for the preparation of BN materials with high quality. It is converted by thermolysis in vacuum at 70 °C into a highly cross-linked polyborazylene ($[B_{2.7}N_{3.0}H_{3.0}]_n$; M_w=4000 g.mol⁻¹) which is transformed into bulk BN materials in high purity at 1200°C in ~ 90% ceramic yield (argon atmosphere) [7]. Such attractive properties (high molecular weight and ceramic yield) result from the high reactivity of B-H and N-H units at low temperature which confer high cross-linking capability to the borazine and latent reactivity to the polyborazylene (cross-linking and chain branching). But, both high cross-linking degree and high capability to cross-link at low temperature disqualify polyborazylene as a candidate for melt-spinning, and therefore for the preparation of fibers.

The first explored route is focused on the chemical modification of molecular precursors, before achieving their thermolysis into preceramic polymers. Borazine-based polymers serve as examples.

As an example, in order to develop the spinnability of borazine-based polymers, the strategy is to substitute highly reactive B-H groups on the pendent borazine unit by less thermally reactive B-R units (Fig. 1), and then perform thermolysis of modified precursors.
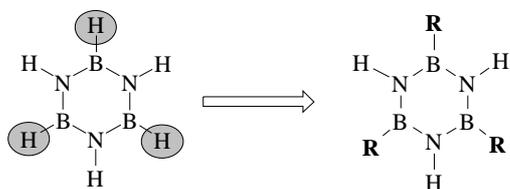
Fig. 1. Chemical functionalization of molecular precursors.

As an illustration, the functionalization of borazine with N(H)CH$_3$ units as R groups yields a molecular precursor, the *B*-(methylamino)borazine, which is thermolyzed in an argon atmosphere (T=185 °C) through major condensation reactions of –N(H)CH$_3$ units into a tractable preceramic polymer, the poly[*B*-(methylamino)borazine] ([C$_{1.9}$H$_{9.1}$N$_{4.4}$B$_{3.0}$]$_n$, n~6.5) with a majority of bridged NCH$_3$ as depicted in Fig. 2 [8,9].

B-(methylamino)borazine   Poly[*B*-(methylamino)borazine]
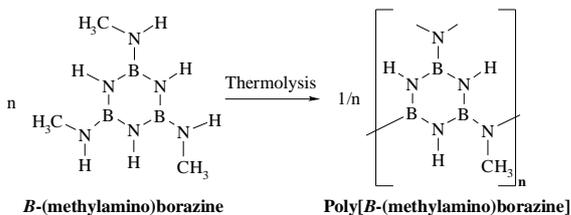
Fig. 2. Conversion of B-(methylamino)borazine into poly[B-(methylamino)borazine] [8,9].

It should be noted that N(H)CH$_3$ ending units are also identified probably due to an incomplete polycondensation.

A typical poly[*B*-(methylamino)borazine] (T$_{thermolysis}$=185 °C) displays a molecular weight around 820 g.mol^{-1} and a ceramic yield of ~56% [8,9]. These decreased values compared with those for polyborazylene result from the absence of reactions between B-H and N-H sites in poly[*B*-(methylamino)borazine]. The lower reactivity of NCH$_3$/N(H)CH$_3$ units reduces the condensation reactions during thermolysis in an argon atmosphere, and therefore the resulting degree of cross-linking of as-synthesized polymers.

3.1.2. Modified C-B-C-bridged polysilazanes – The C-B-C-bridged polysilazanes containing N-methyl units

The tris(dichlorosilylethyl)borane are known as excellent *single-source* precursors for bulk SiBCN materials (Fig. 3) [10,11].
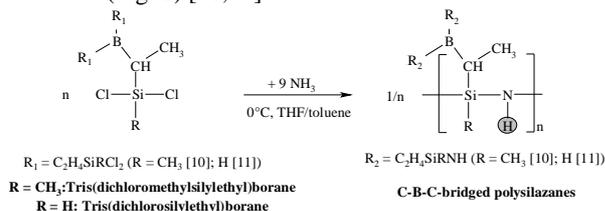

R$_1$ = C$_2$H$_4$SiRCl$_2$ (R = CH$_3$ [10]; H [11])
R = CH$_3$:Tris(dichloromethylsilylethyl)borane
R = H: Tris(dichlorosilylethyl)borane

R$_2$ = C$_2$H$_4$SiRNH (R = CH$_3$ [10]; H [11])
C-B-C-bridged polysilazanes

Fig. 3. C-B-C-bridged polysilazanes of the type [B(SiRC$_2$H$_4$NH)$_3$]$_n$ (R=CH$_3$ [10], H [11].

They are chemically transformed into C-B-C-bridged polysilazanes of the type [B(SiRC$_2$H$_4$NH)$_3$]$_n$ (R=CH$_3$ [10], H [11]) through ammonolysis with ammonia as a linking reagent at 0 °C in toluene or THF. The resulting preceramic polymers generate bulk SiBCN materials in 62% (R=CH$_3$ [10]) and 88% yields (R=H [11]) at 1000 °C (argon atmosphere). The N-H are known to provide polymers with high degree of cross-linking and the addition of Si-H units with latent reactivity in [B(SiHC$_2$H$_4$NH)$_3$]$_n$ induces a thermosetting of the polymer during further pyrolysis by dehydrogenative Si-N coupling [11]. As shown previously, such properties provide high quality bulk ceramics, but poor abilities to produce complex forms of ceramics.

In contrast to the first approach, the second explored route represents a two-step process. It consists to avoid excessive potential cross-linking sites in molecular precursors, and then change the nature of the linking reagent during chemical transformation into polymers. C-B-C-bridged polysilazanes are used as examples.

For example, for designing spinnable C-B-C-bridged polysilazanes, the strategy is to block both reactive Si-H groups of the molecular precursors and N-H of highly cross-linked C-B-C-bridged polysilazanes (Fig. 3) through their substitution by Si-CH$_3$ groups and N-CH$_3$/N(H)CH$_3$, respectively.

For highlighting the influence of pendent groups on cross-linking properties, two modified polymers were prepared by aminolysis reactions of previous molecular precursors (Fig. 3) through the use of methylamine as linking reagent instead of ammonia to yield polymers of the type [B(SiRC$_2$H$_4$NCH$_3$)$_3$]$_n$ in a similar synthesis procedure (0 °C, toluene; Fig. 4) [5,12].

R$_1$ = C$_2$H$_4$SiRCl$_2$ (R = CH$_3$ [10]; H [11])
R = CH$_3$:Tris(dichloromethylsilylethyl)borane
R = H: Tris(dichlorosilylethyl)borane

R$_3$ = C$_2$H$_4$SiRNCH$_3$ (R = CH$_3$ [5,12]; H [12])
C-B-C-bridged polysilazanes containing *N*-methyl units
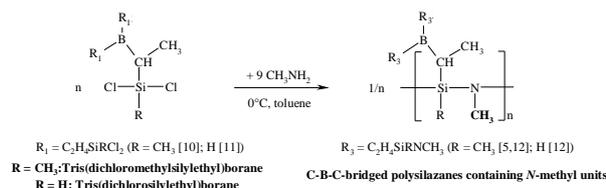
Fig. 4. C-B-C-bridged polysilazanes of the type [B(SiRC$_2$H$_4$NCH$_3$)$_3$]$_n$ (R=CH$_3$ [5], H [5,12].

The cross-linking degree of modified C-B-C-bridged polysilazanes of the type [B(SiRC$_2$H$_4$NCH$_3$)$_3$]$_n$ decreases with the introduction of Si-CH$_3$ and N-CH$_3$/N(H)CH$_3$ groups as reflected in the decreased ceramic yields of such polymers (22%, R=CH$_3$; 68%, R=H) [5,12]. The chemical functionalization at atomic level does not affect the Si:B ratio of polymers ([Si$_3$C$_{14.5}$H$_{36.3}$N$_{4.4}$B$_{1.0}$O$_{0.4}$]$_n$, R=CH$_3$; [Si$_3$C$_{12}$H$_{29.5}$N$_{4.6}$B$_{1.1}$O$_{0.2}$]$_n$, R=H), but inherently increases the proportion in C, N and H compared with ammonolyzed analogs. N(H)CH$_3$ were observed as ending groups suggesting a limited condensation capability of such units.

3.2 Polymer Melt-Spinnability

The melt-spinnability of a polymer can be defined as its ability to be extruded through a spinneret into an

endless filament which is immediately stretched as a fine-diameter endless fiber. The previous chapter showed the possibilities to reduce the rate of cross-linking reactions by the incorporation of appropriate pendent groups with controlled chemical composition. The present chapter shows that the influence of such pendent groups on the melt-spinnability and thermal behavior through thermal (DSC and TMA) and rheological investigations.

3.2.1. Melt-spinnability of poly[B-(methylamino)borazines] - Rheology and DSC experiments

Differential Scanning Calorimetry (DSC) experiments are investigated to follow the thermal behaviour of poly[*B*-(methylamino)borazines] at low temperature. DSC curve (Fig. 5) carried out with a typical poly[*B*-(methylamino)borazine] (M_w~820 g.mol^{-1}) shows that the polymer exhibits a glass transition temperature (T_g) around 85 °C and, in contrast to polyborazylene, neither thermal cross-linking nor decomposition occur in the temperature range 85-200 °C in which the polymer is in the molten state. This behaviour suggests that the presence of N-CH$_3$/N(H)CH$_3$ functions in such polymers lowers the softening point of borazine-based polymers and inhibits thermally-induced cross-linking reactions at low temperature in an inert atmosphere to offer excellent potentialities for a shaping processing in these conditions (low temperature, inert atmosphere).
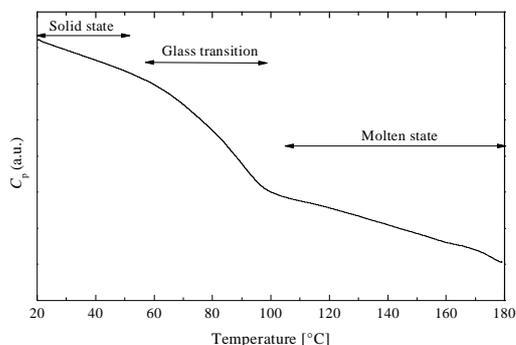

Fig. 5. DSC curve of a typical poly[B-(methylamino)borazine] (M_w~820g.mol^{-1}).

The viscoelastic properties can be measured through rheology experiments. The viscoelasticity is expressed by the viscosity function and additional rheological parameters such as the dynamic moduli G' and G'' as well as the loss tangent tanδ=G''/G' are measured by an oscillatory rheometer. The rheological parameters measured in a dynamic oscillation experiment are carried out in an argon atmosphere for a typical poly[*B*-(methylamino)borazines] (M_w ~820 g.mol^{-1}) in the molten state (>T_g). Results obtained at 175°C are presented in Fig. 6.

The higher values of G'' compared with those of G' suggest the predominant viscous behavior of the polymer

at 175 °C, especially in high frequency rate. Proper melt-spinnability of preceramic polymers is exclusively achieved when both storage modulus (G') and damping factor (tanδ) reach the following conditions: tanδ > 1 and G'$_{min}$<G'<G'$_{max}$. As an appropriate ratio of viscosity to elasticity is necessary to allow fiber formation during extrusion of the polymer and a minimum level of elasticity is required for the fiber to retain its shape upon stretching, a typical poly [*B*-(methylamino) borazine] (M_w ~ 820 g.mol^{-1}) presents an excellent melt-spinnability at 175 °C below ω=10 s^{-1}. This result points to the fact that a poly[*B*-(methylamino)borazines] with M_w ~ 820 g.mol^{-1} and T_g ~ 85 °C can be extruded at 175 °C at a relatively high stretching rate, most probably due to the plasticizing effect of N-CH$_3$/N(H)CH$_3$ units.
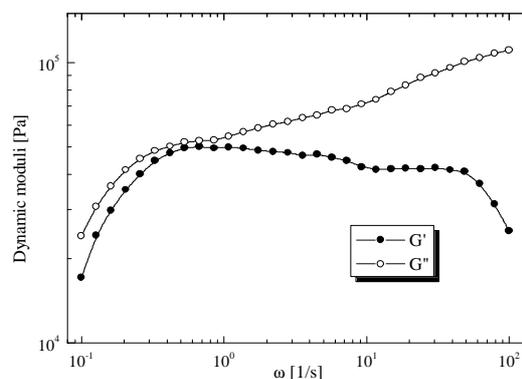
Fig. 6. Dynamic moduli of poly[B-(methylamino)borazines] (M_w ~820g.mol^{-1}) at 175°C.

3.2.2. Melt-spinnability of C-B-C-bridged polysilazanes containing N-methyl units – DSC and TMA

DSC experiments of the modified C-B-C-bridged polysilazanes of the type [B(SiRC$_2$H$_4$NCH$_3$)$_3$]$_n$ (Fig. 4) show that polymers display a glass transition (T_g ~38 °C, R=CH$_3$; T_g ~89 °C, R=H) which is shifted to higher temperature with the presence of Si-H units.

It is clear that the presence of N-CH$_3$/N(H)CH$_3$ units reduces the occurrence of thermally-induced cross-linking reactions leading to the appearance of a softening point upon heating at low temperature. In addition, modified C-B-C-bridged polysilazanes containing Si-CH$_3$ bonds exhibit a certain melt-stability compare to those containing Si-H bonds as shown with Thermo-Mechanical Analysis (TMA) carried out in a nitrogen atmosphere. TMA experiments highlight that the presence of Si-CH$_3$ functions in such polymers offers potentialities for melt-spinnability, since, under load, the polymer [B(SiCH$_3$C$_2$H$_4$NCH$_3$)$_3$]$_n$ melts as observed by the significant decrease in the TMA curve at ~75 °C (Fig. 7). The large dimensional change is stopped around 140 °C.
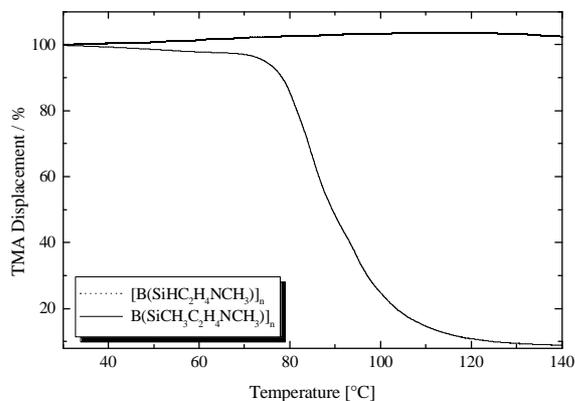
Fig. 7. TMA curves of modified C-B-C-bridged polysilazanes.

In contrast $[B(SiHC_2H_4NCH_3)_3]_n$ is dimensionally stable under load up to 140 °C. This behaviour points to the fact that any polymer melting occurs at low temperature disqualifying $B(SiHC_2H_4NCH_3)_3]_n$ as a candidate for melt-spinning. Because of the sufficient latent reactivity of Si-H units, thermally-induced cross-linking reactions are probably activated. Such polymers build up their molecular weight leading to instabilities during melt-spinning, but to an increased ceramic yield as shown previously. All observations corroborate the fact that the presence of both Si-CH$_3$ and N-CH$_3$ units offer controlled cross-linking properties at low temperature. It is even probable that such pendent groups act as plasticizers during heating at low temperature to lower the softening point and confer appropriate viscoelastic properties to the polymer of the type $[B(SiCH_3C_2H_4NCH_3)_3]_n$.

3.2.3. Melt-spinning process

According to their appropriate viscosity in their molten state (TMA and rheology results), endless green fibers can be obtained from poly[*B*-(methylamino)borazine] and modified C-B-C-bridged polysilazanes of the type $[B(SiCH_3C_2H_4NCH_3)_3]_n$ by melt-spinning into monofilament with adjustable diameters.

High quality green fibers are generated by the continuous extrusion of poly[*B*-(methylamino)borazine] ($T_{spinning}$=175 °C) and C-B-C-bridged polysilazanes of the type $[B(SiCH_3C_2H_4NCH_3)_3]_n$ ($T_{spinning}$=82 °C) followed by the stretching of the endless filament using a rotating spool (Fig. 8(a)). As-spun fibers are flexible, uniform and free of defects (Fig. 8(b,c)).

The melt-spinnability of modified C-B-C-bridged polysilazanes of the type $[B(SiCH_3C_2H_4NCH_3)_3]_n$ highly reflects TMA data (Fig 7, strong load penetration from 75 to 95 °C). The stable melt-viscosity of the polymer allows spinning at a small incremental temperature over the starting of melting (~75 °C).
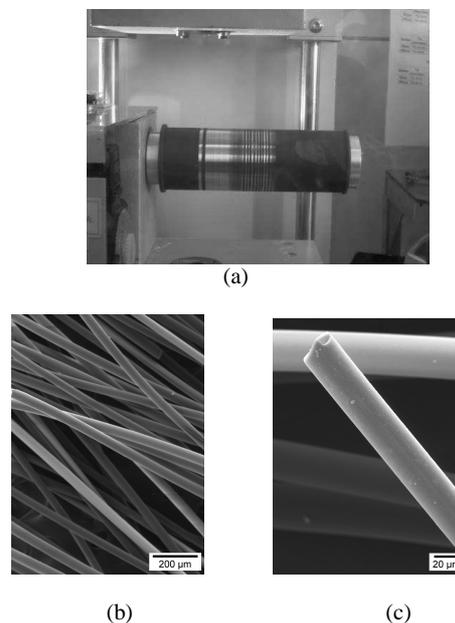

(a)

(b)

(c)

Fig. 8. Melt-spinning process (a). SEM micrographs of resulting green fibers stretched from poly[B-(methylamino)borazine] (b) and [SiCH$_3$C$_2$H$_4$NCH$_3$)$_3$]$_n$ (c) melts.

The poly[*B*-(methylamino)borazine] (M_w~820g · mol^{-1} and T_g~85 °C) also exhibits properties tailored for melt-spinning applications in excellent agreement with rheology data. In accordance with *(i)* its high glass transition temperature which allows take-up of the fiber on the spool at high speed without fiber coalescence and *(ii)* the starting of decomposition around 200 °C in a nitrogen environment, the spinning operation ($T_{spinning}$=175 °C) remains stable and these properties result in *(i)* the preparation of fine-diameter and free of defects green fibers and *(ii)* the reproducibility of the spinning process. With proper stretching, the excellent melt-spinnability of poly[*B*-(methylamino)borazines] is highlighted through the preparation of green fibers with diameters of 15-20 µm.

These spinning behaviours suggest that both a controlled cross-linkage of the polymer and a defined viscoelasticity of the polymer melt are required in order to achieve both a stable spinning process and to get flexible green fibers.

3.3. Polymer-to-Ceramic conversion

The presence of carbon-based pendent groups in the modified polymer should be eliminated through an appropriate process, especially in the preparation of C-free BN fibers. Besides, due to a lower ceramic yield in spinnable polymers, thermally-induced cross-linking reactions should be activated during pyrolytic conversion to prevent loss of fiber integrity.

The two types of as-spun fibers are therefore cured through chemical process involving ammonia as a means to cure fibers, and then pyrolyzed in a controlled

atmosphere to deliver ceramic fibers in the expected composition with retention of the form.

Pyrolysis of the poly[*B*-(methylamino)borazine]-derived cured fibers in an ammonia atmosphere up to 1000 °C followed by a further heat-treatment in a nitrogen atmosphere up to 1800 °C produce white and flexible and circular C-free boron nitride fibers with a B:N ratio 1.2:1. Fibers of ~ 8 µm are provided without loss in fiber integrity (Fig. 9(a)). The polycrystalline nature of the BN fibers is expressed by the coarse-grained microtexture. X-ray diffraction and TEM studies of BN fibers are consistent with the formation of a meso-hexagonal BN phase. Measurements of the mechanical properties of BN fibers give typical tensile strengths of 2.0 GPa and elastic modulus of 440 GPa [13].
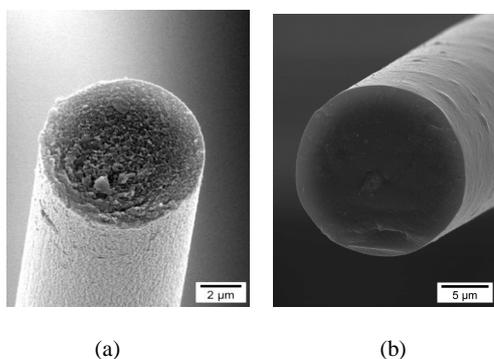

(a)   (b)

Fig. 9. SEM micrographs of BN ceramic fibers (a-b) and SiBCN ceramic fibers (c-d).

Pyrolysis of the cured fibers derived from modified C-B-C-bridged polysilazanes of the type [B(SiCH$_3$C$_2$H$_4$NCH$_3$)$_3$]$_n$ in a nitrogen atmosphere up to 1400 °C produces black and flexible amorphous silicoboron carbonitride ceramic fibers of 10-15 µm (Fig. 10(b)). SEM micrographs show that the microtexture is featureless as a glassy-like material. Chemical composition results show that the initial Si:B ratio (Si:B=3:1) in the molecular precursor is retained in the final ceramic (Si:B = 3:1). Measurements of the mechanical properties of SiBCN fibers give typical tensile strengths of 1.5 GPa and 170 GPa in Young's modulus [5].

4. Conclusions

In this report we have summarized the recent efforts devoted to the preparation of BN and SiBCN ceramic fibers through the Polymer-Derived Ceramics (PDCs) route. Ceramic fibers with designed micro- or nanostructures can be prepared by the chemical tailoring of *single-source* molecular and polymeric precursors. Precursor chemistry allows the design of preceramic polymers with plasticizing pendent groups which yield appropriate viscoelastic and thermal properties to transform the polymers into high-quality fine-diameter green fibers through a stable melt-spinning operation. Such fibers are cured in an ammonia atmosphere without loss in fiber integrity. The subsequent pyrolysis in a nitrogen atmosphere leads to the conversion of as-cured fibers into ceramic fibers in a controlled chemical composition. The PDCs route allows the preparation of metastable solid solutions in fiber form for Ultra-High-Temperature applications.

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