Polymer-derived ceramics route toward SiCN and SiBCN fibers: from chemistry of polycarbosilazanes to the design and characterization of ceramic fibers

Antoine VIARD, Philippe MIELE and Samuel BERNARD

IEM (Institut Europeen des Membranes), UMR 5635 (CNRS-ENSCM-UM), Université Montpellier, Place E. Bataillon, F-34095 Montpellier, France

1. Introduction

Fibrous materials have been used by human for thousand of years in different daily applications (clothes, reinforcement materials, ...). During the last decades, fibers became more technical and their applications extended to more specialized usage especially due to the need for reinforcements in structural ceramic matrix composite (CMC) materials. In the category of technical fibers, refractory ceramic fibers appear to be probably the most appropriate fibrous candidate for new generation prospective engineering composites with a wide range of functional properties meeting user requirements.

Ceramic fibers exist as oxide and non-oxide materials. Oxide-types possess good mechanical properties, chemical and thermal stabilities. They exhibit a polycrystalline microstructure and high values of tensile strength and modulus. In general, they are made of alumina (Al$_2$O$_3$), mixed oxides of Al$_2$O$_3$ and silica (SiO$_2$) leading to mullite, yttrium aluminum garnet (YAG) or zirconium dioxide (ZrO$_2$). Several processing methods are available to produce these fibers: melt-spinning, sol-gel processes, starting from inorganic polymers like polyaluminoxanes, electrospinning... The spinning dopes are generally spun into green fibers and subsequently pyrolyzed in order to remove the possible organic additives (binder) and finally sintered at high temperatures.

Oxide ceramic fibers are commercially available and consist mainly of alumina or mullite. They are supplied by 3M Corporation (Nextel fibers), Sumitomo Corporation (Altex fibers) or Mitsui Mining (Almax fibers) and their cost is relatively low. They are in general used for heat-insulating covers and furnaces. However this type of fibers suffers from grain growth and creep at high temperatures which are limiting factors for long periods of usage. In addition to a lack in long term stability, this type of materials generally does not withstand thermal shocks and suffers from thermal expansion. To overcome these problems, non-oxide ceramic fibers have been considered.

Non-oxide ceramic fibers have been widely used as the skeletal structures in ceramic matrix composites (CMCs) for high-temperature applications where metallic materials and oxide ceramics suffer serious corrosion and mechanical properties deterioration. This is particularly true when considering the drastic working conditions in turbine engines and rocket nozzles which require superior mechanical and chemical properties.

Applications of non-oxide ceramic fibers at industrial level (as-produced or to reinforce matrix composites leading to CMCs) exclusively concerns silicon carbide (SiC)-based fibers. Such fibers are mainly produced in Japan by Nippon Carbon, Co. Ltd. and Ube Industries, Ltd. SiC-based fibers are extremely resistant to wear and high temperatures and are designed to allow much higher operating temperatures in industrial applications than oxide-based fibers. At the same time, they are lighter, more durable and provide damage tolerance by bridging the ceramic matrix (=SiC matrix) cracks that would otherwise cause catastrophic failure in monolithic ceramics. Within this context, SiC fibers represent the best candidate to reinforce CMCs in the next generation of nuclear energy conversion power plants and they...
are more and more applied in brake technologies, as airplane or steam turbines, thereby boosting system efficiency (reduced NOx emissions, reduced specific fuel consumption, increased thrust-to-weight ratio).

A very convenient route to produce non-oxide ceramic fibers is the polymer derived ceramic (PDC) route combined with a spinning-based process as done for polycarbosilane-derived SiC fibers. A wealth of reviews and books have been published on the PDC route\(^1\) as well as on polymer-derived SiC fibers.\(^{15,16,23,24}\) As alternative to SiC fibers, silicon carbide nitride (SiCN) and boron-modified silicon carbide nitride (SiBCN) fibers propose an interesting combination of functional properties and a lower production cost. This is an active topic in the PDC community since 40 years with a production mainly achieved at lab-scale. We felt that it was desirable and timely to present a comprehensive, detailed and critical review of this subject covering developments up to early 2016.

In this review article, we will describe and discuss on the PDC route and its application to prepare PDC fibers by melt-spinning and electrospinning. In particular, the requirements which should be proposed by preceramic polymers to be spinnable will be discussed. This will be followed by an in-depth discussion of the polymer-derived SiCN and SiBCN fibers. One main emphasis of these sections is set on addressing the intimate relationship between molecular structure/architecture of preceramic polymers, their spinning/curing/pyrolysis behavior and the properties of the final fibers. The final section will describe the conclusions. Lastly but not the least, some issues that need to be clarified in the near future are proposed in the conclusion.

2. The PDC route

The Polymer Derived Ceramic (PDC) route finds its starting point back in the middle of the fifties with the published work of Fritz et al.\(^{25}\) relating the formation of Si–C bonds and thus the first conversion of molecular precursors into ceramics. Then, fundamental works in the sixties have focused on the formation of ceramics obtained from polymeric precursors.\(^{26,27}\) These works led finally in the middle of the seventies to the achievement of silicon carbide (SiC) fibers starting from organosilicon precursors (= preceramic polymers).\(^{28,29}\) PCS, a solid, fusible and soluble methyl-substituted polysilanes, namely polycarbosilanes, has been investigated as a precursor for SiC fibers for over 40 years. Three generations of polymer-derived SiC fibers have been developed going from Nicalon\(^{®}\) SiC fibers (1st generation) to Hi-Nicalon-S\(^®\) and Sylramic\(^®\) SiC (3rd generation),\(^{30-36}\) in particular using PCS. This discovery touched off a rapid development of preceramic polymers for i) the preparation of other compositions of fibers\(^{37-42}\) as well as ii) the design of various micro-/nanostructures (amorphous, crystalline or nanocomposites), iii) the production of different ceramic shapes and the development of tailored morphologies (dense or porous) that are difficult, or even impossible to obtain by conventional routes.\(^{43-49}\) This is possible according to the fact that the PDC route may be combined with shaping processes such as dip-coating, extrusion, lithography, casting, pressing or 3D printing.\(^{50-53}\)

The general scheme of ceramic preparation using the PDC route is presented in Fig. 1. As shown in Fig. 1, the first step concerns the preparation of the polymeric precursor (= preceramic polymer) by incorporating the desired chemical groups. A second optional step consists in shaping the polymer via different techniques as listed above depending on the targeted ceramic shape which has to be given. Sacrificial templates may be used during this shaping process to develop the porosity in the final material.\(^{42-50}\) The conversion of the polymer into a ceramic can then be operated in different ways\(^{57-59}\) using different curing/pyrolysis techniques. Another way to proceed to the shaping is to first synthesize fine-grained PDC powders and to shape them afterwards before a sintering treatment.\(^{60,61}\) This is not an exhaustive listing of all possibilities of working with the PDC route but it gives a good overview of the wealth and versatility of this method.

The great advantage of the PDC route lies in its so called “bottom-up” approach. The synthesis of the various ceramics always starts from a molecular precursor (commercially available or home-made) which is subsequently polymerized by reacting with a linking reagent or/and through thermolysis leading to a
polymer we define as preceramic. Before polymerization, the molecular precursor can be modified by incorporation of other elements into its chemical structure or mixed with another molecular precursor. This confers a huge versatility to this approach and allows a large variety of compositions and structures to be generated after pyrolysis, influencing greatly the properties of the ceramics.

Organosilicon precursors such as halogenosilanes made an increasingly important contribution to the research development and manufacture of PDCs and in particular of Si-based non-oxide ceramics.

Chlorosilanes (Fig. 2) are produced by the Müller-Rochow-Synthesis on a large scale. Figure 2 reports the structure of a dichlorosilane R1R2SiCl2 but it should be mentioned that chlorosilanes can be prepared with the final R₅SiCl₄₋ₖ (0 ≤ k ≤ 3) structure depending on the degree of crosslinking and molecular weight targeted. Chlorosilanes are used for the fabrication of polyorganosiloxanes which in turn are the most important inorganic or organometallic polymers.65 Polyorganosiloxanes are generally synthesized by hydrolysis of Si-Cl bonds followed by subsequent condensation of the Si-OH intermediates to form Si-O-Si groups. If ammonia is used rather than water, a similar ammonolysis reaction takes place and silylamines are formed, which can condense to give polysilazanes. Thus, Fig. 3 gives a simplified general description of the structure of polysilazanes [R₁R₂SiNHₙ]₂ prepared from a dichlorosilane R₁R₂SiCl₂. It is assumed that two hydrogen atoms per ammonia molecule are substituted and the chlorine atoms are completely substituted.

The degree of cross-linking/confounding depends on number and nature of Si- and N-bonded substituents as well as on reaction conditions applied. As an illustration, linear or cyclic oligomers as well as linear or cross-linked polymers are formed if R₁ = R₂ = H or CH₃. Si-bonded substituents such as methyl or ethyl are chemically inert and are usually introduced to adjust the needed physical and chemical properties. At the opposite, SiCH₃=CH₂, NH, and SiH groups present in the dichlorosilane (Fig. 2) and/or in the polysilazane (Fig. 3) offer the opportunity to attach supplementary elements to the polymer backbone. Boron, for example, may be introduced by hydroboration of CH₃=CH₂ groups using borane Lewis acid adducts.65-68 In addition, such reactive groups including NH, and SiH units allow the reaction of the polymer with another molecular precursor to modify the latter.65-71 This is the strategy to obtain nanocomposites. It is usually applied to prepare ceramic nanocomposites61-71 but also metal-containing ceramics72-74 in which metallic complexes are first synthesized and then reacted with a polymeric precursor. We may also perform the polymerization of a mixture of molecular precursors to form co-polymers75 or mix two preceramic polymers that react during the pyrolysis.76 Reaction may occur via hydrosilylation (XH + SiCH₂=CH₂; X = Si, Al, B, . . .) and/or dehydrocoupling with formation of X-N units (XH + NH; X = Si, Al, B, . . .).77,78 Preceramic polymer may be also combined with an active (or a reactive) inorganic filler such as a pure, fine-grained metal to form multi-phase components.79 These examples show the large range of possibilities to tailor the composition and nanostructure of ceramics through the investigation of the chemistry of preceramic polymers. It is therefore worth mentioning that properties of PDCs are strongly related to their molecular origin. As a consequence, the molecular structure and chemistry of preceramic polymers has to be tailored to produce ceramics endowed with designed performance properties that reach far beyond those of existing materials. One area that benefits greatly from the development of preceramic polymers is ceramic fibers.

3. The PDC route applied to ceramic fibers

These fibers can be defined as materials in elongated form with a circular section having small diameters (<20 µm), high aspect ratio, good tensile strengths (σ > 2 GPa) and a low density (ρ < 3 g cm⁻³). Production of ceramic fibers from preceramic polymers is based on a four-step sequence for which each step has specific requirements: (1) Synthesis of preceramic polymers from molecular precursors → (2) Spinning of the polymer → (3) Imposed crosslinking (= curing) of green fibers → (4) Pyrolysis of cross-linked fibers into a ceramic object with retention of the imposed fiber shape.

In their initial state, the fiber-forming polymers are preferentially solids and therefore must be first converted into a fluid state for extrusion. This is either carried out by melting without decomposition if the polymer is thermoplastic (melt-spinning) or by spinning the polymer as a solution (solution spinning). If they cannot be dissolved or melted directly as thermosetting polymers, they must be chemically treated to form soluble or thermoplastic derivatives. It should be mentioned that spinning may be assisted with high voltage (= electrospinning). In that case, very thin ceramic fibers can be generated. Melt-spinning and electrospinning are briefly described below.

Melt-spinning is a dry shaping technique i.e. no solvent is required.59,80 In this way, fibers with diameters ranging from a few micrometers to tens of micrometers can be obtained. The typical device (Fig. 4) comprises a tubular furnace ended up with a spinneret composed of one or several capillaries giving the shape to the precursor.

The polymer is inserted into the heating chamber to be molten and is then pushed through the furnace with a piston (or a gas) in order to be extruded through the spinneret.

The filament thus formed is then stretched around a collecting spool in rotation. Between the spinneret and the spool the polymer is allowed to cool down and stiffen in order to keep the
The stretching of the fiber can affect the orientation of the polymer chains within the fiber and can result in better organized ceramic structures. Different parameters can be varied during the spinning:

- Furnace’s temperature
- Piston’s velocity (or applied pressure)
- Spinnneret’s geometry
- Distance spinnneret – spool
- Spool velocity

The temperature in the furnace allows adjusting the rheological behavior of the precursor. The piston’s velocity determines the extrusion’s rate but also the applied pressure which is directly connected to the shear stress. The geometry of the spinnneret acts on the shape of the fiber and on the dimension of the extruded filament. The distance between the spinnneret and the take up spool influences the solidification of the polymer while the spool velocity has an impact on the diameter of the fibers.

The choice of the polymeric precursor is a crucial point for melt-spinning. Indeed, general requirements have to be considered to ensure the processability of preceramic polymers. As an illustration, Laine et al. defined some ideal properties for a polymeric SiC precursor in order to be able to obtain high-performance fibers by melt-spinning. These prerequisites can be extended to the production of fibers from any type of organosilicon polymers.

Firstly, the purity of the precursors impacts the purity of the related ceramics and therefore, their properties. As a consequence, the chemistry behind the synthesis must be well understood and controlled.

High molecular weights are desired to restrict the volatilization of low molecular weight oligomers during the pyrolysis which participates to the degradation of the shape. The organization of the structure is a key point for developing the spinnability of preceramic polymers. Linear polymers (structure A, Fig. 5) with high molecular weight are expected to produce fibers. Indeed, the linearity of the polymeric chain should increase the spinnability of the polymer by improving its fusibility. However, Yajima observed that the high molecular weight of linear polydisilacyclobutane rendered their spinning extremely complex. More precisely, precursors are expected to exhibit non-Newtonian fluid properties in order to be correctly extruded but they have to present in the same time a relatively high viscosity at zero shear so the green fibers are self-supporting.

The thermal conversion of preceramic polymers into ceramic materials is accompanied by the formation of gaseous byproducts and therefore mass loss is observed during the polymer-to-ceramic conversion. An efficient crosslinking ability to avoid the depolymerization of spinnable polymers during the ceramization and a suitable ceramic yield associated with a limited increase of the density limit the volume change occurring during the conversion of the precursor into ceramics. This will allow retaining the fiber integrity during pyrolysis. As a consequence, precursors are expected to be composed of reactive functions enabling further chemical reactions to render the polymer infusible and therefore to keep the shape during the pyrolysis. Various ways exist to render the green fibers infusible, for example the use of γ-rays or electronic irradiation causing radical reactions (i.e. surface cross-linking or hardening, not recombination), or through an air- or ammonia-curing.

Finally, the evolution of the ceramics microstructure must promote a good densification of the material or delay crystallization. However, controlling these various requirements and combining them in only one polymer remains an ambitious objective to prepare fibers by melt-spinning. Compromises are usually needed.

Electrospinning is another technique of fibers production. The principle of this process is to align the polymer’s chains along an electrical field leading to the formation of fibers (Fig. 6). Resulting fibers exhibit diameter between a few nanometers and a few micrometers. This process is quite easy to set up since it only requires a generator for powerful electrical fields, a syringe pump, a spinnneret which can consist in a non-beveled needle and an electrically conductive collector (aluminum foil for example).

The polymer is preferentially solubilized in a solvent and loaded inside a syringe connected to a metallic needle. The solution is then pushed through the needle by applying a high electrical field between the needle and the collector. This electrical field will induce the electrical loading of the drop coming out from the needle and causes its conical deformation (Taylor’s cone) due to the electrostatic forces. When the electrical field is strong enough to overcome the surface tension, a solution jet is emitted toward the collector. The solution jet is stretched continuously and the solvent evaporates during the path between the needle and the collector, leading to the formation of fibers onto the collector.

This technique allows a good control of the fibers geometry which formation is governed by several parameters. First of all holes, i.e., capillaries, thus forming continuous filaments during the further spinning step. More precisely, precursors are expected to exhibit non-Newtonian fluid properties in order to be correctly extruded but they have to present in the same time a relatively high viscosity at zero shear so the green fibers are self-supporting.

![Fig. 5. Different structures proposed by Wynne and Rice to improve the spinnability of preceramic polymers.](image)

![Fig. 6. Electrospinning principle.](image)
the polymer has to be soluble in a conductive solvent. The polymer concentration and the solvent choice have to be made wisely in order to control the spinning process. Furthermore, the viscoelastic properties of the preceramic polymer have to be tailored. Usually, a high molecular weight organic polymer is required to be added to the preceramic polymer. Concerning the operating parameters, namely the applied tension, the solution flux and the distance between the needle and the collector, they have to be set in order to meet good conditions for the obtaining of fibers.

In the following sections, we will describe the implementation of the melt-spinning to prepare SiCN and SiBCN fibers. Then, we will focus on the application of electrospinning to prepare these materials at nanoscale.

4. SiCN ceramic fibers

Polymer-derived SiC fibers, which are currently commercially available, are an example of the success in combining expertise in polymer chemistry, materials science and engineering for the development of a commercial scale fiber manufacturing process. An important key for the production of a polymer-derived SiC fiber is an ultra-fine microstructure, which allows high-tensile strength.28 Their creep and thermal resistance are primarily determined by the stoichiometry and specifically the oxygen content. SiC fibers are the main focus in the thematic of polymer-derived ceramic fibers but the high cost of PCS caused by expensive raw materials, elaborate synthesis processes and low volume production, is clearly one of the limitations of SiC fibers.

Cost for polysilazanes is on a significantly lower level. Polysilazanes are Si3N4 precursors and have been considered in the past as fiber precursors according to the fact that Si3N4 exhibits good mechanical properties with a very high hardness and chemical inertness. The Si3N4 fiber production process was very similar to that developed by Yajima et al. Curing was achieved in air but the pyrolysis was conducted under ammonia atmosphere leading to the formation of SiNO fibers.94 This oxygen content has then been reduced by employing irradiative curing of the green fibers.95

Perhydropolysilazane (PHPS, [SiH2–NH]n) is a highly reactive preceramic polymer containing two Si–H and N–H functions in its structure.45,96–99 Through pyrolysis under nitrogen, PHPS leads to a composite material composed of a majority of Si3N4 and around 13 wt % of silicone (Si).100,101 PHPS was considered as fiber precursor as reported by Aylett,102 Seyfert96,103 and Isoda.104 However, PHPS-derived Si3N4 crystallized readily above 1200–1300°C with catastrophical effects on the thermal stability and performance of fibers leading to a catastrophic drop of the mechanical properties.105,106 Through these studies, it appeared that the control of the grain growth in Si3N4 fibers has to be considered in the preparation of high temperature stable non-oxide ceramic fibers from polysilazane.

As shown previously, the final product composition, the phase selectivity, the crystallinity and therefore the properties of Si-based non-oxide ceramic fibers may be engineered by controlling the molecular architecture of polysilazanes and by changing the nature of the R groups linked to Si (Fig. 3). Linking alkyl groups to Si allows introducing carbon in the Si3N4 network and producing SiCN ceramics.75,105–113 One interesting property of the polymer-derived SiCN ceramics is that they remain amorphous up to 1400–1500°C in inert atmosphere. They also exhibit excellent oxidation and creep resistance at very high temperatures because of the absence of metal oxide additives.106,111 These findings indicate that the amorphous SiCN ceramics are good candidates for high-temperature applications.

SiCN fibers were reported for the first time in the beginning of the seventies.112 Two compounds, trichloromethylsilane and dichloromethylsilane, were mixed together with methylamine in order to form an oligosilazane which was then converted into a polycarbonasilazane by means of a heat treatment. This polymer was subsequently shaped to produce green fibers which were then pyrolyzed to generate ceramic fibers exhibiting homogeneous mixture of Si, C and N elements and eventually oxygen. This work inspired a lot of studies to prepare SiCN fibers. In one of these studies,119 tris(N-methylamino)methylsilane was polymerized at 520°C to deliver a polymer that could be melt-spun between 220–250°C. Fibers were hand drawn by touching the surface of the melt with a glass rod and stretching the polymer. As-obtained green fibers were then cured in a humidity conditioned chamber at 100°C and pyrolysis followed at 1200°C under nitrogen atmosphere. The resulting ceramic fibers showed mechanical properties comparable to those of SiC fibers and a high electrical resistivity.

These materials inspired industries, in particular Wacker Chemie AG.120 Dichlorodiorganosilane, dichloromethylsilane and hexamethyldisilazane were reacted together at temperatures between 350 and 450°C to generate the polycarbosilazane precursor. Green fibers with diameter between 5 and 50 μm were produced by melt-spinning around 150°C. The curing process was performed under oxidative atmosphere at temperatures between 20 and 200°C to render the fibers insusible and the pyrolysis was then done under inert gas at temperature higher than 1100°C. The obtained ceramic fibers were composed of SiC and Si3N4 phases but also small amounts of SiO2 and carbon.

A great comprehension of the properties of the SiCN fibers has been brought by Naslain et al.115,119 The synthesis of the starting precursor was done within a two steps process.115 In a first step a polylsilazane (PSSZ), a co-polymer, was synthesized by adding dropwise dimethyldichlorosilane and 1,3-dichloro-1,2-dimethylsilazane to a suspension of sodium in boiling toluene. PSSZ was formed by a reductive coupling (dehalogenative cross-coupling) with a suspension of sodium at toluene reflux (Fig. 7). To ensure the reaction of all Si–Cl bonds, ammonia was bubbled in the solution afterwards at 0°C. In a second step the PSSZ precursor was heated up to be converted into a melt-spinnable polycarbosilazanes (PCSZ) according to a two step process. It was firstly synthesized by heating PSSZ at 335°C and then taking an aliquot fraction of the resulting product to be heated to 372°C. Melt-spinning was used to produce the green fibers and the conditions of spinning were chosen to obtain fibers with a mean diameter of 25 μm.122 Different compositions of filaments were produced through pyrolysis treatment at...
1200°C, including SiCN(O) fibers with a curing step under oxidative atmosphere and SiCN filaments with a curing step under inert atmosphere by irradiation with γ-rays. SiCN(O) fibers exhibited failure strength of 1.85 GPa and a stiffness of 185 GPa after pyrolysis at 1200°C. The curing step affected the pyrolysis process and the properties of the resulting fibers. In fact, an optimal oxygen-curing temperature of 140°C was found to be necessary in order to prevent defects on the fibers and to increase the mechanical properties. SiCN fibers with diameter around 16 μm were obtained. Fibers presented high thermal stability under nitrogen atmosphere: they underwent only minor change in composition and structure up to 1400°C. At 1600°C, a complete degradation of fibers occurred: a very thin carbon skin formed and tiny β-SiC crystals grew within a SiCN amorphous matrix most probably due to the carothermal reduction of silicon nitride. The fibers exhibited stiffness of 220 GPa and a failure stress of 2.4 GPa at room temperature which remained almost constant after ageing treatments at 1600°C under nitrogen.

The oxidation stability of PCSZ-derived fibers was compared to SiC fibers derived from polycarbosilane (PCS). It was shown that the layer forming on top of the PCSZ-derived fibers is thinner and that the rate limiting step is a diffusion controlled mechanism which could be the mass transfer of oxygen through the silica layer. This indicated a better resistance to oxidation compared to PCS-derived SiC fibers.

Another important place of research regarding SiCN fibers is located at the Institute of Ceramic Materials Engineering, University of Bayreuth, Germany. Motz et al. produced huge amount of work related to SiCN fibers starting with the development of a synthesis method for a SiCN precursor called ABSE. Its chemical formula is shown in Fig. 8.

ABSE precursor was obtained from dichloromethylsilan and dichloromethylvinylsilan. A first step of hydrosilylation led to the formation of ethylene-bridged crystalline bis(chlorosilyl)-alkane. Ammonia was then bubbled in the toluene solution to incorporate NH groups and form the polysilazane network. ABSE is a solid polymer which consists of connected ethylene-bridged cycles without any reactive functions like Si–H and Si-vinyl groups. However, ABSE possesses a low molecular weight directly following synthesis that is unsuitable for the melt-spinning process. Thermal and catalytic aftertreatment is necessary to increase the molecular weight of the ABSE precursor and to improve the rheological properties of the melt with regard to viscoelasticity. With greater molecular weight, the viscosity increased and the elastic response of the melt to shear deformation intensified. ABSE fulfilled the most important requirements for melt spinning including high melting point, thermal stability, and stretchability as well as suitable viscosity in the molten state. Indeed, the non-Newtonian behaviour of the polymer melt (shear thinning) enabled a stable, continuous melt-spinning process and lead to green fibers with improved mechanical properties and a diameter of 20–30 μm (withdrawal speed 500 m/min). The ethylene-bridges are the reason for the excellent stretchability, and the 5-membered cycles involved thermal stability of the molten polymer up to 170°C for several hours. Further cross-linking only took place via condensation of ammonia at temperatures higher than 200°C.

Different curing processes were tested by employing very reactive organic compounds or electron irradiation. In fact the lack of reactive sites in ABSE is here disadvantageous for curing, but a short time irradiation with electron beam dose of 200 kGy is enough. Pyrolysis treatment at 1300°C in nitrogen atmosphere led to the formation of SiCN ceramic fibers. They exhibit a tensile strength of 1.1 GPa which can be improved by 50% by adding 0.5 wt% carbon nanotubes to the polymeric precursor.

Later on, the same group reported the use of commercial polysilazanes, ML33 and HTT1800 (Fig. 9), from Clarant Advanced Materials GmbH (Sulzbach, Germany).

The liquid ML33 polysilazane is the product obtained by ammonolysis of dichlorodimethylsilane and dichloromethylsilan (Fig. 9). The liquid HTT1800 polysilazane is synthesized by ammonolysis of dichloromethylvinylsilan and dichloromethylsilan (Fig. 9). Because of their liquid state, these polymers may be applied in shaping processes including, casting, polymer infiltration and pyrolysis (PIP), spray-, dip- and spin-coating and resin transfer moulding. In contrast, they could not be directly used to prepare fibers by spinning techniques. Within this context, authors proceeded to a partial crosslinking of these two precursors to render them melt-spinnable. To do this, tetra-n-butylammoniumfluoride (TBAF) has been added dropwise to the solution containing the polymers dissolved in THF. TBAF acted as a catalyst to selectively crosslink the polymers via the N–H and Si–H groups while calcium borohydride played the role of an inhibitor of the reaction. Catalysts concentration and time of reaction impacted the final chemical and physical properties what makes it possible to synthesize spinnable precursors. Polymer batches with high molecular weights (~10000 g mol⁻¹), a defined glass transition temperature (Tg) between 65 and 81°C and a viscoelastic melt-behaviour enabled the spinning into green fibers with a regular shape and less defects. Subsequent curing was achieved by electron beam. It was shown that the quality of the resulting ceramic fibers after a pyrolysis at 1100°C in flowing nitrogen depends on the selective crosslinking of the polymers.

Very recently, these precursors have been employed for processing thick ceramic fibers as an alternative to CVD SiC monofilaments to be used in a new generation of metallic matrix composites. The same process was used for fibers preparation and enabled the production of fibers with diameters larger than 70 μm. Compared to ML33-derived green fibers, HTT-derived green fibers required a lower dose of electron beam due to the presence of reactive vinyl groups ensuring a high degree of crosslinking. After pyrolysis of the green fibers at 1100°C under nitrogen, SiCN fibers with large diameter are obtained as shown in Fig. 10. Diameter of the fibers inherently influences the tensile strength. A value of 0.8 GPa is measured for fibers with diameter smaller than 70 μm whereas it reached 1.6 GPa for fibers with diameter larger than 70 μm.

Polysilazane-derived SiCN fibers displayed not only higher oxidation stability, but also an affordable price in comparison...
SiCN ceramics have higher thermal stability compared with the binary Si$_3$N$_4$ or SiC amorphous ceramics, derived from carbon-free or nitrogen-free silicon-based preceramic polymers, respectively. After pyrolysis to 1000°C, the microstructure of these amorphous materials can be generally described as a random Si–C–N network composed of tetrahedral mixed units, [SiC$_x$N$_{4-x}$] (1 ≤ x ≤ 4), whose relative volume fraction depends on the composition of the starting precursor. Their amorphous network is retained up to around 1440°C, temperature at which SiC and Si$_3$N$_4$ crystals as well as graphite-like domains are formed. The presence of Si$_3$N$_4$ crystals and graphite-like domains involves carboconversion reactions above 1440°C and formation of SiC as well as nitrogen causing the significant decrease of the mechanical properties of SiCN fibers. The addition of boron to the Si–C–N system is well reported to shift the temperature at which carbothermal reduction occurs. This is an important step to keep the fiber stable during high temperature processes. The preparation of polymer-derived SiBCN fibers is the object of the next part of the present review.

5. SiBCN ceramic fibers

The presence of reactive units like SiCH=CH$_2$, NH or SiH groups in dichlorosilanes (Fig. 2) and/or polysilazanes (Fig. 3) makes it possible to incorporate additional elements in the chemical structure of the fiber precursor. This is, in general, the strategy applied to fabricate SiBCN fibers.

Adding boron at molecular scale to SiCN ceramics, i.e., leading to boron-modified silicon carbonitride (SiBCN) ceramics, advantageously modifies some of the properties of the Si–C–N system. SiBCN ceramics display an amorphous inorganic network and exhibit atomically homogenous elemental distributions. Their main interest is the stability of their amorphous network at very high temperature because B(C)N layers surrounding Si$_3$N$_4$ grains prevent the carboconversion of the latter as it occurs in SiCN ceramics above 1440°C. However, the stability of the amorphous state is closely dependent on the preceramic polymer architecture and chemistry.

The first synthesis of a SiBCN polymeric precursor has been reported in 1985. The preceramic polymer consisted in two different structural monomeric units as indicated in Fig. 11. One monomer units consisted in Si–C bonds in the backbone while the second one was composed of B–N bonds.

To synthesize the precursor, a polysilane and B-trimethyl-N-triphenylborazine were mixed together and heated up to temperatures between 250 and 500°C for 1 to 10 h. It was postulated that the two types of compounds bridged together by heating according to polycondensation reactions. The rheological behavior of the polymeric precursor could be adjusted depending on the starting reactants and on the reaction conditions. Green fibers could then be produced by melt-spinning or dry-spinning. In order to render the filaments insulfibe a curing step was performed after spinning either by heating in an oxidative atmosphere for several hours at 100–200°C or by exposing the green fibers to γ-rays or electron beam. Pyrolysis of the fibers was done by slowly heating to temperatures between 1000 and 1600°C under nitrogen atmosphere. The resulting ceramic fibers displayed an average diameter of 11 μm and showed a tensile strength of 3 GPa and a Young’s modulus of 200 GPa. SiBCN (Silicon Nitride/Silicon Carbide) fibers are then produced by melt-spinning from this resin and cured under inert atmosphere at 1600°C under nitrogen atmosphere. The resulting ceramic fibers showed an average diameter of 11 μm and a tensile strength of 1.6 GPa. The fracture surface of a large diameter ceramic fiber obtained from HTT.144

![Fracture surface of a large diameter ceramic fiber obtained from HTT.144](image)

Fig. 10. Fracture surface of a large diameter ceramic fiber obtained from HTT.144

Constitutive monomers of the precursor developed by Takamizawa et al.148

![Constitutive monomers of the precursor developed by Takamizawa et al.148](image)

Fig. 11. Constitutive monomers of the precursor developed by Takamizawa et al.148

Another way to proceed to the fabrication of SiBCN fibers has been developed by Lu et al.150,151 Dimethyldichlorosilane (Me$_2$SiCl$_2$) and dichloromethylsilane (MeHSiCl$_2$) were mixed together in a given ratio and ammonia was added to the solution. The product of this co-ammonolysis was then heated in a nitrogen gas flow at a given temperature to form the polysilazane which was then melt-spun to obtain green fibers. These fibers were then cured successively in boron trichloride and in ammonia. The curing treatment allowed the incorporation of the boron element into the polymer’s structure. Pyrolysis was then performed in nitrogen atmosphere at 1250°C to obtain ceramic boron-containing SiCN fibers.

A few years later, Chu et al.152 developed a method based on the use of a hybrid precursor consisting of a blend of a polyborosilazane (PBSN) and a polycarbosilane (PCS). PBSN constituted 10 wt% of the blend and was synthesized by a polymerization process of silazane oligomers involving boron trichloride. Green fibers were produced by melt-spinning and were cured in air before pyrolysis at 1250°C. Ceramic fibers showed an average diameter of 15.6 μm and a tensile strength of 1.6 GPa.
transition temperature was more stable in the case of the PIN-HPZ precursor which was consequently selected for further studies.

The synthesis of the precursor was done via mixing of the HPZ and the PIN-H and subsequent heating of this mixture at 60°C for several hours. The resulting material was finally distilled under vacuum at 95°C. Green PIN-HPZ-derived fibers with an average diameter of 35 µm were obtained by melt-spinning. The curing of the polymer fibers was performed by a brief exposure to trichlorosilane followed by moist air in order to form a silica layer around the fibers. Pyrolysis was finally carried out in an argon atmosphere at 1200°C leading to the formation of black dense and uniform ceramic fibers as shown in Fig. 14. Unfortunately mechanical testing of the fibers was not possible mainly due to the lack of a sophisticated spinning device.

As a crucial point, the performance of SiBCN ceramics depends strongly on the homogeneity of the preceramic polymer, and co-condensation of different molecular or polymeric precursors is unfavourable as shown previously. This induces phase separation and decomposition of the ceramics into its binary phases at a lower temperature compared with preceramic polymers prepared from single-source precursors which already contain the electropositive elements in the ratio desired for the final ceramics. The second strategy consisted in the synthesis or use of a molecular precursor which reacted with a linking reagent to generate a polymer containing all ceramic elements.

There are two main single-source polymeric systems that lead to SiBCN ceramics. The first synthetic pathway pioneered by Riedel et al. focused on the synthesis of boron-modified polysilazanes of the type \( \text{[B(C}_2\text{H}_4\text{SiCH}_3\text{NH})_3]_{\text{n}} \).\(^{147}\) They represent polysilazane rings which are cross-linked via -C-B-C- bridges. The second approach proposed by Jansen et al. makes use of the synthesis of polyborosilazanes, i.e., polysilazanes cross-linked via -B-N-B- bridges.\(^{157}\)

Jansen et al. proposed an original synthesis procedure as depicted in Fig. 15 to develop melt-spinnable polymers. First hexamethylsilazane and silicon tetrachloride were stirred together at room temperature. The resulting compound was then added dropwise to boron trichloride at \(-78°C\) to form trichlorosilyliminodichloroborane (TADB). The chlorine groups of TADB could then react by either ammonolysis or aminolysis. Ammonolysis (reaction with ammonia) led to unmeltable precursor while aminolysis (reaction with methylamine) yielded thermosetting oligomers which can then be polymerized in a controlled manner by varying temperature and reaction time.\(^{158}\)

Green fibers were subsequently produced by melt-spinning or dry-spinning. In this case curing was not a necessary step since extensive crosslinking of the polymer took place during the shaping. Nevertheless chemical curing could also be performed by exposing fibers to trichlorosilane what is often preferred for kinetic reasons.\(^{159}\)

Heat-treatment at 1500°C under nitrogen atmos-
The polymer in order to control its rheology. To do this, the ammonolysis step involving ammonia in the procedure of Riedel et al. has been replaced by an aminolysis step with methylamine as depicted in Fig. 16. The N-bonded methyl groups played a major role in the processability of the polymer by limiting the progress of the condensation reactions. The obtained boron-modified N-methyl polysilazane exhibited a large glass-transition temperature allowing the production of fibers by melt-spinning.

However the main problem with this polymeric precursor was the very low ceramic yield avoiding the retention of the shape of the green fibers upon pyrolysis. To overcome this problem, a curing process was developed by heating the green fibers at 200°C under an ammonia atmosphere. Transamination reactions occurred to render the polymer infusible. Pyrolysis was then performed under nitrogen atmosphere at 1400°C resulting in the formation of SiBCN fibers with an average diameter of about 23 μm as shown in Fig. 17. The fibers exhibited a tensile strength of 1.3 GPa and a Young’s modulus of 172 GPa. The ceramic fibers retained their amorphous character until 1700°C. XRD patterns only showed very broad signals indicating the nucleation of nanometric grains of silicon carbide.

Further research works concerning this type of precursor were conducted by studying the structure of the polymer and the influence of the synthesis conditions. The synthesis of the precursor requires an addition of 9 molar equivalent of methylamine compared to TDSB to react with all chlorine functions and to form the salt which can then be filtered. This molar ratio of methylamine (MA) compared to TDSB was varied and it appeared that the amount of methylamine added has a strong effect on the rheology of the final polymeric precursor. Indeed a ratio between 9 and 9.2 of MA:TDSB is needed in order to obtain a polymer with suitable rheological properties and stability for melt-spinning.

Through a detailed investigation of the polymer-to-ceramic conversion, fibers with average diameter of 12.1 μm, tensile strength of 1.4 GPa and Young’s modulus of 120 GPa were obtained through the optimization of the synthesis procedure.

Other methods for SiBCN precursors syntheses within one step appeared in the last years. Lee et al. developed a method which is more or less identical with that of Jansen, without purification of the intermediate product. It consisted in the mixing of hexamethyldisilazane with boron trichloride and trichlorosilane and subsequent heating of the solution at 200°C. Unfortunately this polymeric precursor could not be spun into fibers which motivated research works by Tang et al. Trichlorosilane was replaced by dichlorosilane in order to achieve a lower degree of crosslinking which allowed the spinning of polymer fibers with...
heptamethyldisilazane (HpMDZ) was used instead of hexamethyldisilazane due to the dehydrogenation reaction. For these reasons in polymers which cannot be spun at higher temperature than 70°C, the dehydrogenation of Si-H and N-H bonds occurred readily under moderate conditions contributing therefore to the quick polymerization of the precursor while a too high degree of crosslinking should be avoided. Moreover, the simultaneous presence of both of these groups resulted in the formation of polymer droplets during the electrospinning. Therefore, a small amount of PEO (polyethylene oxide) was added into the solution enabling the electrospinning of polysilazanes (modified by heteroelements or not) is rather limited as shown below.

Starting from a commercial available polysilazane precursor to produce SiCN-based ceramic fibers by electrospinning is a cost effective process. With this aim in mind, Zhai et al. developed a production route using Ceraset VL20 as polysilazane. This oligosilazane is liquid with a low viscosity and therefore, it could not be directly used for electrospinning. As a consequence, it was first modified with aluminum tri-sec-butoxide to form a polyaluminasilazane precursor. However the insufficient chain overlap resulted in the formation of polymer droplets during the electrospinning. Therefore, a small amount of PEO (polyethylene oxide) was added into the solution enabling the fiber formation. Different mixtures with various ratios of chloroform and less volatile N,N-dimethylformamide were used as solvents. This ratio had an influence on the size and on the surface morphology of the electrospun polymer fibers. The nonwoven mat was then pyrolyzed under argon atmosphere at 1000°C resulting in an aluminum-modified silicon carbonitride (SiAlCN) ceramic mat with very low oxygen content.

The same group also worked on the incorporation of multi-walled carbon nanotubes (MWCNTs). MWCNTs were dispersed in CH3Cl with a block copolymer (poly(3-hexylthiophene)-b-poly [poly(ethylene glycol) methyl ether acrylate]) which was then added to the polyaluminasilazane and the PEO. The electrospinning of this solution produced polymer fibers with well aligned CNTs which were then converted into SiAlCN fibers through an appropriate heat treatment at 1000°C under argon atmosphere. These fibers exhibited an enhanced electrical conductivity compared to the SiAlCN bulk sample.

The precursor used in the previous study cannot be electrospun without any additional polymer, PEO in this case. In fact, a majority of works focused on electrospinning of preceramic polymer is based on the mixture of the latter with an organic polymer that provide the viscoelastic properties to the solution.

Recently Jansen et al. published their work concerning the
electrospinning of SiBCN precursors without the use of organic parts.\textsuperscript{177} For this purpose dichloroboryl-methyl-trichlorosilyl-amine (DMTA) was synthesized in a similar way that the TADB precursor developed by the same group and presented earlier in the present paper (Fig. 18).

The subsequent aminolysis of this compound led to the obtaining of an air-sensitive viscous liquid polymeric precursor. This synthesis was then followed by a thermal treatment of the product in order to increase the viscosity of the polymer through cross-linking reactions.

The resulting polymer has then been dissolved in an adjusted amount of mixed dichloromethane and pentane to achieve an adequate viscosity enabling the electrospinning process to be carried out. A subsequent curing step under ammonia at room temperature was necessary to render the fibers infusible and preserve the structure during the pyrolysis which was performed at 1400°C under argon atmosphere. The electrospun fibers were successfully converted into ceramic SiBCN felts with fibers showing a mean diameter of 2.2 μm as depicted in Fig. 19. A further decrease of the fibers diameter could be expected by lowering the viscosity of the spinning solution even if this seemed to induce the formation of beads.

The group also proceeded to the functionalization of the felts by depositing SnO\textsubscript{2} using chemical vapor deposition (CVD). The obtained heterostructures showed an increase of the conductivity as well as a higher specific surface area and smaller pore sizes. Tests were conducted to show the potential application of these materials as electrode materials in gas sensing.

7. Conclusion

The Polymer-Derived Ceramics (PDCs) route has been developed as a promising alternative to the conventional powder route. In particular, it represents the method of choice to design non-oxide ceramic fibers. This route is based on the SiC fibers process published by Japanese researchers in 1976. This discovery touched off a rapid development of preceramic polymers for the preparation of fibers in various compositions, mainly based on silicon. Herein, the major developments of the last 40 years in the research field of silicon carbonitride and boron-modified silicon carbide fibers have been discussed. These materials attracted much attention due to their outstanding properties in terms of thermal stability, mechanical properties such as high tensile strength and good creep resistance but also because of their interesting oxidation resistance even at high temperatures.

Fibers may be produced using melt-spinning and electrospinning processes. This required many efforts in the development of polymeric precursors with homogeneous chemical structures and optimal rheological behavior allowing an easy spinning. This has been in the center of numerous research works to be able to produce high quality and defect free fibers. Once spinning has been performed, a curing process is applied to render green fibers infusible. It can be achieved by γ-rays or electronic irradiation or using reactive atmospheres such as air or ammonia. After curing, the pyrolysis achieves the conversion into ceramics. The polymer-to-ceramic transformation process involves a complex sequence of chemical changes that are truly multidisciplinary. The control of the chemistry during the solid-state thermal decomposition of polymers through the design of the intermediate steps (to convert the polymer system into an inorganic intermediate) and the use of annealing treatments (to change the inorganic intermediate into the desired final nanostructure) must be done with full understanding to generate materials capable of performing in demanding conditions. Amorphous, multicomponent ceramics are generated and the main objective is to keep this amorphous state at very high temperature to retain the properties of the fibers. This in general demonstrated with SiCN and SiBCN fibers using single-source precursors.

8. Future prospects

The good performances of SiCN and SiBCN ceramic fibers as well as their limited cost point them as a good alternative to currently more widely used SiC fibers for reinforcement applications. This is illustrated through the Matech company (Westlake Village, California) which commercializes SiCN fibers with funding from the US Navy (NAVAIR, Patuxent River, MD). However improvements in terms of mechanical performance and reproducibility of these performances are still needed and the main studies at lab-scale are firstly focused on the synthesis process and spinability of preceramic polymers to elaborate high performance and cost-effective SiCN and SiBCN ceramic fibers. The second research focus is to develop the functionality of SiCN and SiBCN ceramic fibers. One of the objectives could be the development of integrating functionalities into these fibers, i.e. by conferring them electrical, magnetic or catalytic properties. Within this context, the European Membrane Institute of Montpellier (France, Dr. Samuel Bernard) in collaboration with the Institute of Ceramic Materials Engineering of Bayreuth (Germany, Prof. G. Motz) are both involved in the ANR-DFG project carbofibers dealing with multifunctional non-oxide ceramic fibers through incorporation of transition metals into the chemical structure of the starting polymeric precursors. This project falls within the scope of the growing interest coming from industries concerning fibrous reinforcements for CMCs.

Acknowledgements The authors gratefully acknowledge the funding agency Agence Nationale de la Recherche (ANR) which supports the work through the PolyCeramMem project (Projet ANR-13-BS08-009).

References
1) F. Wallenberger, S. Dunn and N. Weston, SAMPE Quarterly (Society of Aerospace Material and Process Engineers); (USA), 21 (1990).


