

Polymer-Derived Ceramics: 40 Years of Research and Innovation in Advanced Ceramics

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Preceramic polymers were proposed over 30 years ago as precursors for the fabrication of mainly Si-based advanced ceramics, generally denoted as polymer-derived ceramics (PDCs). The polymer to ceramic transformation process enabled significant technological breakthroughs in ceramic science and technology, such as the development of ceramic fibers, coatings, or ceramics stable at ultrahigh temperatures (up to 2000°C) with respect to decomposition, crystallization, phase separation, and creep. In recent years, several important advances have been achieved such as the discovery of a variety of functional properties associated with PDCs. Moreover, novel insights into their structure at the nanoscale level have contributed to the fundamental understanding of the various useful and unique features of PDCs related to their high chemical durability or high creep resistance or semiconducting behavior. From the processing point of view, preceramic polymers have been used as reactive binders to produce technical ceramics, they have been manipulated to allow for the formation of ordered pores in the meso-range, they have been tested for joining advanced ceramic components, and have been processed into bulk or macroporous components. Consequently, possible fields of applications of PDCs have been extended significantly by the recent research and development activities. Several key engineering fields suitable for application of PDCs include high-temperature-resistant materials (energy materials, automotive, aerospace, etc.), hard materials, chemical

engineering (catalyst support, food- and biotechnology, etc.), or functional materials in electrical engineering as well as in micro/nanoelectronics. The science and technological development of PDCs are highly interdisciplinary, at the forefront of micro- and nanoscience and technology, with expertise provided by chemists, physicists, mineralogists, and materials scientists, and engineers. Moreover, several specialized industries have already commercialized components based on PDCs, and the production and availability of the precursors used has dramatically increased over the past few years. In this feature article, we highlight the following scientific issues related to advanced PDCs research:

- (1) General synthesis procedures to produce silicon-based preceramic polymers.
- (2) Special microstructural features of PDCs.
- (3) Unusual materials properties of PDCs, that are related to their unique nanosized microstructure that makes preceramic polymers of great and topical interest to researchers across a wide spectrum of disciplines.
- (4) Processing strategies to fabricate ceramic components from preceramic polymers.
- (5) Discussion and presentation of several examples of possible real-life applications that take advantage of the special characteristics of preceramic polymers.

Note: In the past, a wide range of specialized international symposia have been devoted to PDCs, in particular organized by the American Ceramic Society, the European Materials Society, and the Materials Research Society. Most of the reviews available on PDCs are either not up to date or deal with only a subset of preceramic polymers and ceramics (e.g., silazanes to produce SiCN-based ceramics). Thus, this review is focused on a large number of novel data and developments, and contains materials from the literature but also from sources that are not widely available.

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Feature

I. Introduction to polymer-derived ceramics (PDCs)

SINCE the 1960s, silicon-based PDCs have been synthesized directly by the pyrolysis of organosilicon polymers.¹ More than 11 182 papers have been published about “precursor ceramics” but only 835 have been denoted as PDCs (Fig. 1), which are the focus of this feature article.^{2–11} In this review, we will concentrate our attention mainly on silicon-based PDCs. Other classes of PDCs will be briefly acknowledged.

In the early 1960s, Ainger and Herbert,¹² Chantrell and Popper¹³ reported the production of nonoxide ceramics starting from molecular precursors. Ten years later, Verbeek and colleagues^{14–16} presented for the first time the polymer to ceramic transformation of polysilazanes, polysiloxanes, and polycarbosilanes in order to produce small-diameter Si₃N₄/SiC ceramic fibers for high-temperature applications. Significant progress in the science of PDCs was achieved by Fritz and Raabe¹⁷ and almost at the same time by Yajima *et al.*^{18,19} on the synthesis of SiC ceramic materials by the thermolysis of polycarbosilanes.

The polymer precursors represent inorganic/organometallic systems that provide ceramics with a tailored chemical composition and a closely defined nanostructural organization by proper thermal treatment (curing and thermolysis processes) under a controlled atmosphere. The PDCs route is an emerging chemical process as attested by the increasingly commercial development of preceramic polymers to produce near-net shapes in a way not known from other techniques.²⁰

Moreover, PDCs are additive-free ceramic materials possessing excellent oxidation and creep resistance up to exceptionally high temperatures. The most known classes of PDCs are in the binary systems Si₃N₄, SiC, BN, and AlN, ternary systems SiCN, SiCO, and BCN as well as in the quaternary systems SiCNO, SiBCN, SiBCO, SiAlCN, and SiAlCO. In recent years, several pentanary systems of PDCs have been reported as well.

The traditional method to prepare ceramics involves powder technology, which, however, requires the presence of sintering additives and significantly constrains technical applications. In the case of the PDCs route starting from preceramic polymers, ceramic fibers, layers, or composite materials can be produced, which cannot be easily obtained using the powder technology. In principle, preceramic polymers can be processed or shaped using conventional polymer-forming techniques such as polymer infiltration pyrolysis (PIP), injection molding, coating from solvent, extrusion, or resin transfer molding (RTM). Once formed, objects made from the preceramic polymers can then be converted to ceramic components by heating to temperatures high enough to consolidate the elements contained in the polymer structure to a ceramic.

Precursor-derived covalent ceramics in general exhibit enhanced thermo-mechanical properties with respect to creep and oxidation, crystallization, or phase separation up to 1500°C and

higher. Recent investigations have shown that in some special cases, namely in boron-containing SiCN ceramics, the high-temperature stability in terms of decomposition can reach 2200°C. The relatively low synthesis temperature (lower energy consumption) of 1100°–1300°C for the production of PDCs is of economical interest, in comparison with classical ceramic powder processing technology, which requires 1700°–>2000°C to sinter covalent Si₃N₄- and SiC-based ceramics. Moreover, binary Si₃N₄ and SiC cannot dissolve carbon or nitrogen, respectively, to form ternary SiCN compositions. Similarly, SiO₂ and SiC cannot dissolve carbon or oxygen to produce SiCO ceramics. So far, the ternary SiCN and SiCO varieties can only be synthesized using the molecular approach discussed here.

Because of this property profile, PDCs have been studied for their use as structural ceramics for high-temperature applications over the last few years. For instance, polymer-derived silicon carbonitride (SiCN) ceramics were found to exhibit creep (under compression) and oxidation resistance even at temperatures between 1000° and 1500°C.^{21,22} However, in the case of a formal carbon excess in the SiCN materials, a solid-state reaction of carbon with silicon nitride to form silicon carbide and nitrogen can occur at $T > 1450^\circ\text{C}$.^{23,24} Polymer-derived silicon boron carbonitride materials (SiBCN) have remarkably higher thermal, chemical, and mechanical (creep) stability than that of the boron-free counterparts even at temperatures up to 2000°–2200°C in an inert atmosphere. Their extraordinary thermal stability is believed to rely on kinetic rather than on thermodynamic reasons. Structural disorder in SiBCN ceramics, which results in increased free activation energies of both crystallization and the solid-state reaction of the Si–N bond with carbon, is considered to be responsible for the thermal stability of these materials.²⁵

II. Preceramic Polymer Synthesis

The molecular structure and type of the preceramic polymer influences not only the composition but also the number of phases as well as the phase distribution and the microstructure of the final ceramic produced therefrom. Thus, the macroscopic chemical and physical properties of PDCs can be varied and adjusted to a huge extent by the design of the molecular precursor. Therefore, synthesis of preceramic polymers is one of the key issues in the field of PDCs.

The success of synthesizing silicon-containing PDCs such as silicon carbonitrides and oxycarbides (SiCN and SiCO) can be attributed to the strong bonding between silicon and carbon in the polymeric compound preventing carbon from volatilizing in the form of small hydrocarbon molecules during pyrolysis in controlled inert environments.^{1,2} PDCs can be synthesized at relatively low temperatures. Complete pyrolysis and thus transformation of the silicon-based polymer to the ceramic occurs at or below 1100°C.^{3,4}

An oversimplified general formula of an organosilicon polymer suitable as a precursor for the synthesis of ceramics is presented in Fig. 2. There are two important parameters to modify and design the preceramic compound on the molecular level: firstly, the group (X) of the polymer backbone and, secondly, the substituents R¹ and R² attached to silicon. The variation of (X) results in different classes of Si-based polymers such as poly(organosilanes) with X = Si, poly(organocarbosilanes) with X = CH₂, poly(organosiloxanes) with X = O, poly(organosilazanes) with X = NH, and poly(organosilylcarbodiimides) with X = [N = C = N] (see Panel A).

By changing the functional groups R¹ and R² at the silicon atoms, the chemical and thermal stability as well as the solubility

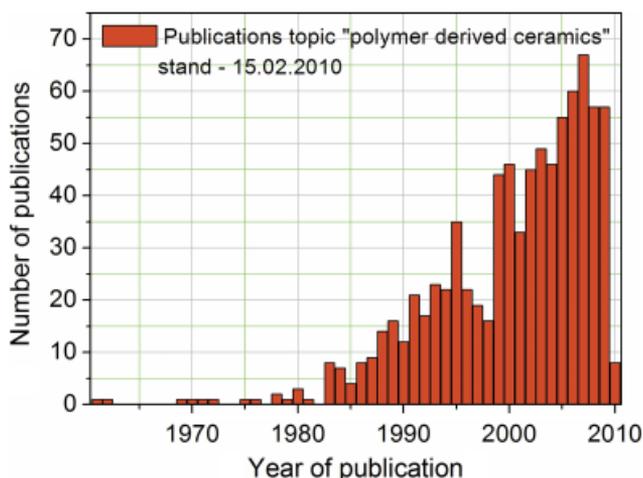


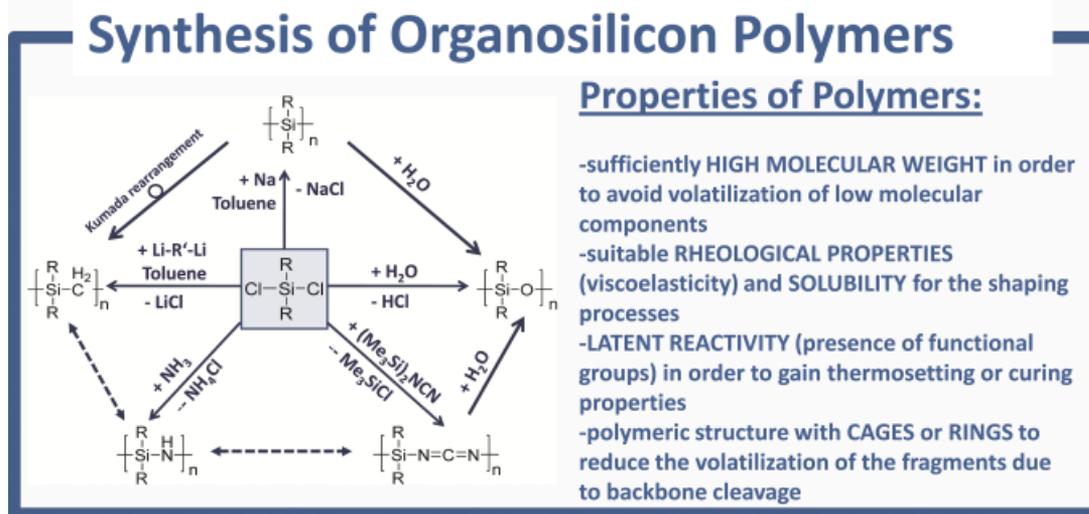
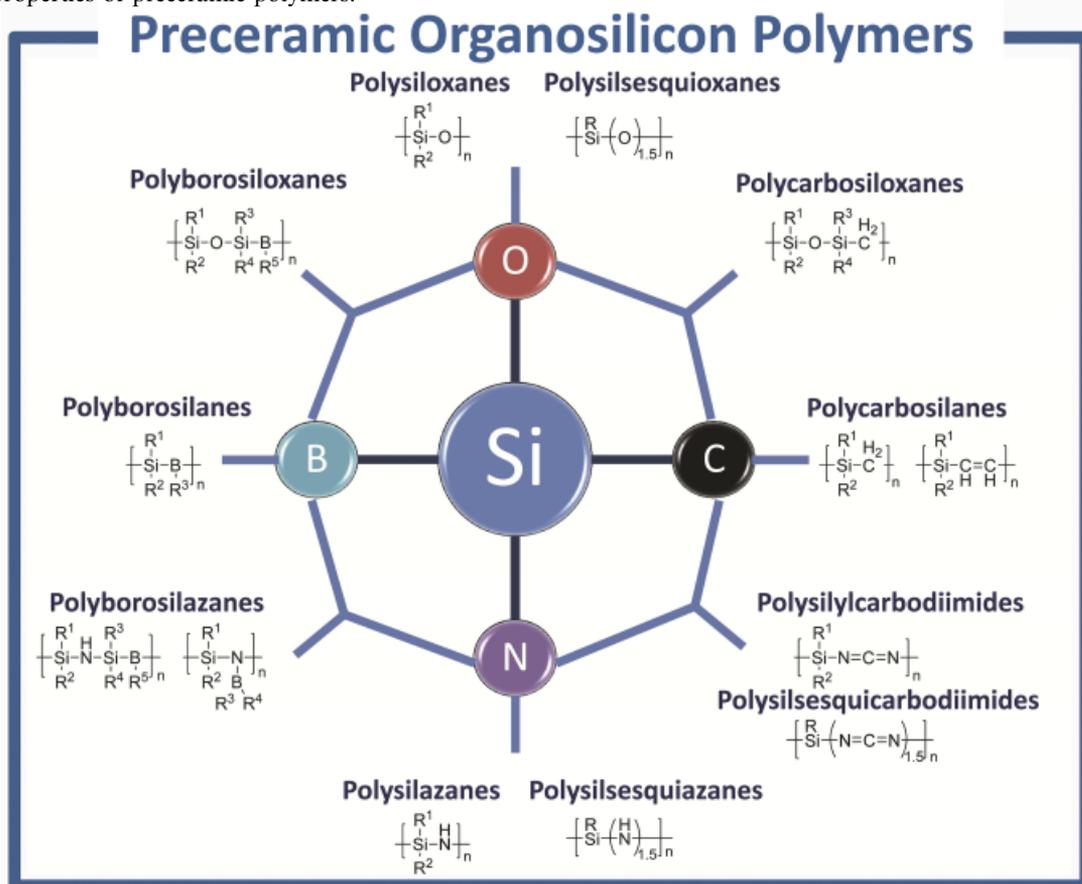
Fig. 1. Number of publications resulting from a search with the keyword “polymer-derived ceramic”, from 1961 up to now.



Fig. 2. General oversimplified representation of the molecular structure of preceramic organosilicon compounds.

Panel A. Types and Synthesis of Preceramic Polymers

1. Main classes of Si-polymer as precursors for ceramics;
2. Synthesis route to silicon-based preceramic polymers starting from chlorosilanes;
3. Desired properties of preceramic polymers.



of the polymer, their electronic, optical, and rheological properties can be modified and adjusted. Usually, hydrogen or aliphatic or aromatic organic side groups R are attached at the silicon atoms. In particular, the solubility, the thermal stability, and the viscosity as a function of the temperature are important features for the further processing of the polymers. Moreover, organic substituents as the side groups R control the carbon content in the ceramic derived therefrom.

In order to be competitive with traditional ceramics, the preceramic polymer has to be either cheap or the synthesis has to be

selective to form products with a novel composition and exceptional or unusual properties. Up to now, several review articles and books related to the synthesis of polysiloxanes, polysilanes, and poly(carbosilanes)^{22,26} have been published.

The syntheses of the most representative classes of Si-polymers from organochlorosilanes are shown in Panel A. The production of organosilicon polymers is strongly facilitated by their well-known chemistry and reaction-controlled thermolysis. Several alternative routes for the synthesis of the molecular preceramic compounds are reported. The educts for the process can

be chlorosilanes, hydrosilanes, vinylsilanes, and alkenylsilanes, which enable polymerization by means of elimination, substitution (metathesis), or addition reactions. The chlorosilanes R_xSiCl_{4-x} ($x = 0-3$; R = organic side group) are the most frequently used starting compounds because of their commercial availability and their low cost. Chloro-organosilicon compounds are important starting materials for the synthesis of polysilanes, poly(carbosilanes), poly(organosilazanes), poly(borosilazanes), poly(silylcarbodiimides), poly(silsesquioxanes), poly(carbosiloxanes), and other silyl-containing polymers as shown in Panel A.^{14,27-44}

In the present paper, we will focus our attention only on the basic classes of Si-based polymers, namely poly(organocarbosilanes), poly(organosiloxanes), poly(organosilazanes), and poly(organosilylcarbodiimides), the rest of them already being described in many recent papers.^{21,22}

There are some requirements for preceramic polymers in order to be effective for the thermal decomposition process (Panel A). The polymers should possess a sufficiently high molecular weight in order to avoid volatilization of low-molecular components; they should have appropriate rheological properties and solubility for the shaping process and latent reactivity (presence of functional groups) for the curing and cross-linking step.

One of the characteristics of PDCs is to incorporate up to large quantities of carbon in silicon oxide- and nitride-based phases. The presence of organic side groups allows the control of the amount of carbon in the ceramic. Formerly, it was assumed that excess carbon in PDCs is detrimental with respect to mechanical and high-temperature properties (resistance to crystallization and oxidation). However, in recent years, it has emerged that, under certain conditions, high carbon-containing SiCO and SiCN ceramics exhibit high resistance toward crystallization and decomposition.⁴⁵⁻⁴⁹

(1) Poly(organosilanes)

Poly(organosilanes) are composed of a Si-Si backbone and organic substituents attached to the silicon atoms. They have been generating attention lately because they exhibit photo-conductivity, luminescence, and other functions as well as high thermal stability. These properties originate from the so-called σ conjugation.^{18,26,50-53}

The polysilanes have found applications as functional materials, e.g. as semiconductors, photoresists, hole-transporting materials, and as precursors for silicon carbide-based ceramics.^{54,55} The first synthesis of a poly(diphenylsilane) by a Wurtz-like coupling reaction of diphenyldichlorosilane with sodium in toluene was reported in 1921 by Kipping.^{56,57} Up to the 1970s, several soluble homo- and copolymers were published.⁵⁸⁻⁶⁰ Despite all the synthetic advances in the chemistry of polysilanes,^{26,61-68} the old Wurtz-type reductive dehalogenation reaction remains the most general and common procedure for the synthesis of this type of polymers.⁶⁹⁻⁷² Besides the Wurtz coupling reaction, an alternative method for the production of polysilanes is the catalytically dehydrogenative oligomerization of hydrosilanes in the presence of transition metal complexes as reported by Aitken *et al.*^{73,74}

(2) Poly(organocarbosilanes)

The first approach for the synthesis of poly(organocarbosilanes) from poly(organosilanes) was reported by Kumada and colleagues. This reaction is based on the thermal reorganization of a poly(methylsilane) to yield the polycarbosilane and is well-known as the Kumada rearrangement.⁷⁵

Several polycarbosilanes are presently commercially available.

In Fig. 3, different types of poly(organocarbosilanes) that can be used as precursors for β -SiC-related ceramics are shown.⁷⁶⁻⁸² The general formula of poly(organocarbosilanes) is shown here in an oversimplified way. Most poly(organocarbosilanes) have in fact a much more complex structure containing Si-C and Si-Si bonds, hyperbranched structures, and so on. Depending on the

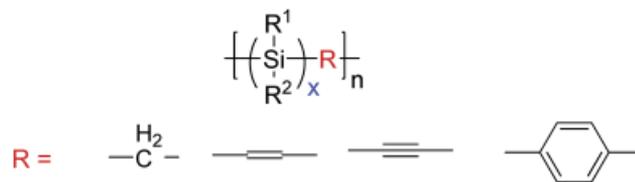


Fig. 3. General types of poly(organocarbosilanes) (oversimplified representation).

structure of the carbosilane chain, different ceramic yields are obtained. Interested readers should refer to the literature cited above, for more specific details.

Polymers possessing an alternating arrangement of a π -conjugated unit⁸³ such as phenylene,⁸⁴ ethynylene,⁸⁵⁻⁸⁷ and a sil(an)ylene unit in the backbone were synthesized by coupling reactions,^{86,88} thermal cyclopolymerization^{89,90} and a variety of ring-opening polymerization (ROP) reactions including anionic,⁹¹⁻⁹⁵ thermolytic, and catalytic coordination techniques,⁹⁶ each with some limitations.

The most important application and at the same time the most extensive studies were conducted in the area of SiC-based fibers⁹⁷ starting from poly(methylcarbosilane), namely PCS-[MeHSiCH₂]_n- and PMCS (PCS with metal M = Ti, Zr, Al). Most ongoing research on SiC-based fibers utilizes polycarbosilanes as the precursor because of its high ceramic yield.

(3) Poly(organosiloxanes)

Poly(organosiloxanes) are important construction materials and are widely used for sealing applications. They are generally denoted as silicones and are usually inexpensive and a great variety of derivatives is commercially available. Many of them have excellent chemical, physical, and electrical properties.⁹⁸⁻¹⁰² The general synthesis method for the preparation of polysiloxanes comprises the reaction of chloro(organo)silanes with water as presented in Panel A.

In recent years, novel silicon-rich poly(organosiloxanes), namely polysilaethers,¹⁰³ have been synthesized by the polycondensation of α , ω -functionalized linear silanes¹⁰⁴⁻¹⁰⁶ and by the ROP of cyclic silaethers.^{107,108} These hybrid materials combine the properties of polysilanes with those of polysiloxanes (Fig. 4).

Interesting "nanoblock" preceramic polymers are the branched poly(organosilsesquioxanes) [RSi-O_{1.5}]_n.¹⁰⁹⁻¹¹¹ As shown in Fig. 5, the polysilsesquioxanes can have different configurations.

Recently, several studies on carbon-rich SiCO ceramics derived from polysiloxanes showed that these materials have enhanced stability against crystallization and high-temperature resistance than originally anticipated.⁴⁵⁻⁴⁹ Carbon-rich ceramics can be defined as materials in which the content of carbon is exceeding 20 wt%.

(A) *Sol-Gel Synthesis of Polysiloxanes:* Cross-linked polysiloxanes or silicon resins can also be prepared by the sol-gel process through hydrolysis and condensation reactions of

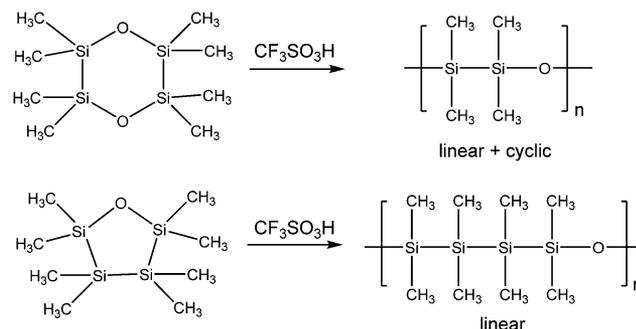


Fig. 4. Synthesis of polysilaethers by ring-opening polymerization.

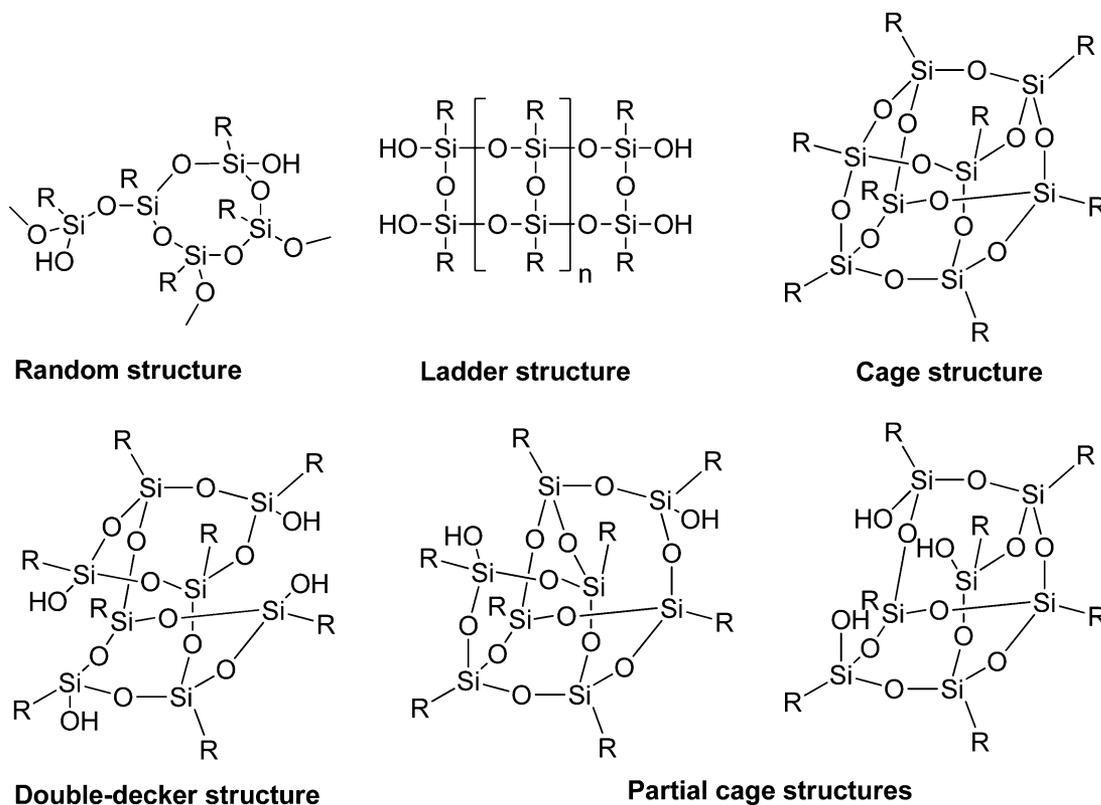


Fig. 5. General types of poly(organosilsequioxanes).

hybrid silicon alkoxides. This route was used by the first researchers who opened the field of silicon oxycarbide glasses.^{112–114} The precursors are organically modified silicon alkoxides of the general formula: $R_xSi(OR')_{4-x}$, which, after gelation lead to the corresponding silicon resins $R_xSiO_{(4-x)/2}$. R is an alkyl, allyl, or aryl group and R' is usually a CH_3 or C_2H_5 . The sol-gel process allows a precise control of the composition of the starting silicon resin by cohydrolysing different hybrid silicon alkoxides: accordingly precursors for stoichiometric, excess-C or excess-Si SiCOs, have been prepared.¹¹⁵ Moreover, with this method, extra elements, such as Al, Ti, or B, can be homogeneously introduced in the preceramic network via the corresponding metal alkoxides.¹¹⁶ The drawbacks of the sol-gel process are the poor control of the viscosity, which prevents the use of many shaping technologies such as extrusion, or injection molding and the high volumetric shrinkage during drying which makes the production of crack-free samples not straightforward.

(4) Poly(organosilazanes)

The first preparation, classification, and characterization of silazanes and polysilazanes was reported in 1885, followed by several other reports up to 1957.^{117–120} These and the following studies resulted in a large number of mostly cyclic oligosilazanes and have been summarized in several review articles.^{22,121–123} In the 1950s and 1960s, the synthesis of oligo- and polysilazanes as potential siloxane analogues as well as precursors to prepare silicon (carbo)nitrides and related materials was reported.^{124–127} Today, the interest in silazanes primarily derives from their applications as silylating agents in synthetic chemistry and as single-source precursors for the preparation of ceramic materials by vapor-, liquid-, and solid-phase pyrolysis.¹²¹

The ammonolysis of organosilicon chlorides as a method for the synthesis of poly(organosilazanes) was published first in 1964 by Krüger and Rochow.¹²⁸ Almost 10 years later, Verbeek and colleagues^{14–16} reported on the production of small diameter ceramic fibers from polymeric carbosilazanes. Their work

opened up the area of research in the production of polysilazanes as precursors for ceramics.^{14,121,129–139}

As also shown in Panel A, the synthesis of polysilazanes can be made by ammonolysis reactions of chlorosilanes with ammonia or by aminolysis with different primary amines, both methods having the difficulty of separation of the polymeric reaction product from the solid byproducts, NH_4Cl or H_3NRCI .¹⁴⁰

High ceramic yields are generally obtained from high-molecular-weight polymers. In order to increase the molecular weight of the poly(organosilazanes) and also to enhance the degree of cross-linking, several methods have been proposed. Extensive activities have been devoted to the modification of silazane oligomers into nonvolatile precursors. The first approach was reported by Seyferth and colleagues in 1984 and consists in using KH basic catalyst for the deprotonation of N–H group adjacent to an Si–H group in a poly(organosilazane).^{141–143} Another interesting approach was proposed by Laine and colleagues when the silazane oligomers were cross-linked in the presence of transition-metal complexes.^{144,145} Also, the modification of silazane oligomers with urea or isocyanate-containing compounds has been reported to improve the chemical and physical properties of the silazane precursors. Seyferth and colleagues reacted *cyclo*- $[CH_3Si(H)NH]_n$ derived from ammonolysis of CH_3SiHCl_2 and urea in different molar ratios and synthesized poly(ureidosilazane)s.^{146,147} Moreover, Schwark and colleagues reacted methylvinylsilazane cyclic oligomers with isocyanates and synthesized poly(ureamethylvinyl)silazanes (PUMVSs).^{148–151} The products were found to exhibit a wide range of viscosity, depending on the amount of isocyanate (2–6 wt%) added.

Presently, a series of polysilazane derivatives is commercially available. They are used as precursors for SiN_x dielectrics, as antigraffiti coatings and as precursors for the synthesis of high-temperature resistant silicon carbonitride (SiCN)-based ceramics. The most prominent polysilazane series is now produced by KionCorp (Columbus, OH), a ClariantBusiness^{152,153} and comprises the following commercial derivatives: Polysilazane HTT 1800, Ceraset[®] Polysilazane 20, and Ceraset[®] Polyureasilazane.

(5) Poly(organosilylcarbodiimides)

The second class of precursors that yield SiCN ceramics upon thermal decomposition consists of poly(organosilylcarbodiimides) (with X = NCN). They are air-sensitive polymers and exhibit enhanced thermal stability as compared with the analogous polysilazanes (X = NH or NR).^{22,154–160} The early work on the synthesis of silylcarbodiimides (since 1960s^{161–166}) was summarized in a comprehensive review article published by Gordetsov et al.¹⁶⁷ The first poly(silylcarbodiimides) containing alternating Si–N = C = N– units were synthesized by Pump and Rochow¹⁶⁸ and 3 years later by Klebe and Murray.¹⁶⁹

Several studies^{166,170,171} have shown that bis(trimethylsilyl)carbodiimide ($R_3Si-N=C=N-SiR_3$, with R = CH₃) itself is an efficient starting material for the synthesis of other element carbodiimides simply by its reaction with organoelement halides as well as with pure element halides as shown in Panel A.^{166,171–178}

In 1997, Riedel and colleagues published the first thermal transformation of poly(organosilylcarbodiimides) to SiCN ceramics.^{155,157,172,179} As a method for the synthesis of SiCN ceramics, the carbodiimidolysis of chlorosilanes (R_xSiCl_{4-x} , with $0 \leq x \leq 2$) is a one-step salt-free reaction under inert atmosphere, is catalyzed by pyridine and it uses inexpensive educts and has quantitative yields.¹⁵⁵ Starting from dichloro (organosilanes), cyclic or linear poly(silylcarbodiimides) are formed, while organo(trichlorosilanes) provide highly branched poly(silsesquicarbodiimides)^{155,157,158,180,181}. The reaction of tetrachlorosilane with $R_3Si-N=C=N-SiR_3$ (R = CH₃) and subsequent heat treatment of the highly cross-linked polymer results in the direct formation of the ternary carbonitrides SiC₂N₄ and Si₂CN₄.¹⁷²

Recently, air-stable linear carbon-rich polysilylcarbodiimides $-[R^1R^2Si-NCN]_n-$ with R¹ = phenyl, R² = Ph, Me, H, vinyl have been reported.¹⁸² The increase of the carbon content in these precursors induces a raise of the carbon content in the final ceramics, which is due to the side groups R¹ and R². The high carbon content of the precursors enhances the thermal stability of the SiCN ceramic derived therefrom and increases the temperature of crystallization.¹⁸² Moreover, crystallization of Si₃N₄ is inhibited.

The current research is progressing toward developing new synthetic strategies to produce cheap and novel functionalized silicon-based polymers and to clarify the relationship between their molecular structure and the materials properties of the final ceramic. In conclusion, the thermolysis of Si-based polymers under defined atmosphere and heat-treatment conditions is a simple and inexpensive additive-free process that allows to control and to adjust the microstructure and thus the materials properties of ceramic components just by choosing the appropriate organosilicon polymer, as discussed in the following “Sections III and IV.”

The synthesis of β-containing organosilicon polymers is not discussed here since their production is already reported in several paper and books.^{21,183}

III. Processing of Preceramic Polymers

(1) Shaping and Cross-Linking

A specific characteristic of preceramic precursors is that they are polymeric in nature at the temperature at which they are shaped into components. Therefore, they can be subjected to a large variety of different forming methods, some of them unique or at least much more easily exploitable for polymers than ceramic powders or pastes. Furthermore, this approach has important technological advantages over the use of other molecular precursors, such as sol–gel ones, as preceramic polymers do not have any drying problems that hamper the possibility of fabricating bulk components, do not need long processing times for gelation and drying, do not require flammable solvents, can be processed in the molten state, their solutions are stable in time and, at least for cheap, commercially available polysiloxanes,

they do not require any specialized handling procedures. On the other hand, sol–gel precursors, which have been extensively used to fabricate SiOC-based ceramics, are also well suited for using liquid-forming technologies to fabricate coatings, fibers, aerogels and for impregnating different matrices, and they can be loaded with fillers to obtain multicomponent ceramics.¹⁸⁴

An example of the advantage of using preceramic polymers is that machining before ceramization avoids the problems connected to tool wear and brittle fracture upon finishing of the component.¹⁸⁵ Also, when using preceramic polymers for joining, the precursor effectively binds together the parts at low temperature, therefore making handling before heat treatment much simpler.¹⁸⁶ Plastic forming technologies (RTM, warm pressing, fiber drawing, extrusion, and injection molding, etc.) can be all applied to preceramic polymers; for example spinning of thin fibers can be achieved easily, and the rheological characteristics of the precursor can be tailored by modifying its molecular architecture.¹⁸⁷ Siloxanes have been saturated with supercritical CO₂, a process industrially used for the fabrication of microcellular plastic components, and then ceramized to produce highly porous foams.¹⁸⁸ Ceramic matrix composites are often fabricated using the PIP process, which is significantly faster and more environment friendly than chemical vapor infiltration (CVI).¹⁸⁹ The possibility of creating nanostructures (wires, belts, tubes, etc.) directly during the pyrolysis of catalyst-containing preceramic polymers is also something that is unique to these materials,¹⁹⁰ as the formation of a large amount of transient porosity during the polymer-to-ceramic conversion, which can be exploited to create superior adsorbent materials.¹⁹¹ Furthermore, preceramic polymers can be liquid or solid, depending on their molecular architecture and weight; if solid, they can be dissolved in several organic solvents or can be molten at low temperatures (usually < 150°C). This often leads to components possessing finer details, in comparison with powder-based systems.

Table I lists the shaping techniques applied in recent years and reported in the scientific and patent literature. They can all be grouped into the same processing categories applicable to ceramic materials in general, i.e. casting/solidification, deformation, machining/material removal, joining, and solid freeform-ing.¹⁹²

Typically, a precursor that is either a cross-linkable liquid, or a meltable and curable solid, or an unmeltable but soluble solid is used. A specific requirement for processing components using preceramic polymers is that, after shaping, the part needs to be transformed into a thermoset capable of retaining its shape during ceramization. The incorporation of suitable functional groups (e.g., Si–H, Si–OH, or Si–vinyl functionalities) enables the formation of a thermoset via condensation or addition that occur spontaneously, typically, below 200°C (thermal cross-linking). The cross-linking temperature can be lowered by using catalysts, with the additional benefit of avoiding the evaporation of oligomers with formation of bubbles and increasing the ceramic yield.^{250,251} Bubble formation during curing can be eliminated using an overpressure applied using a silicone oil medium²⁵² or gas. The introduction of a catalyst often also allows for the cross-linking reactions to occur during shaping and not the subsequent pyrolysis treatment. It should be pointed out, though, that the extent of cross-linking strongly affects the rheological behavior of a preceramic polymer, and therefore it has to be carefully controlled especially when plastic forming technologies are used.²⁵³ Selective laser curing has also been successfully applied to fabricate parts with a high degree of morphological complexity by rapid prototyping.²¹⁷

Curing can be achieved after shaping as well, by different means besides simple heating. The method most used in the past was oxidative curing, which, however, leads to significant oxygen contamination (~ 15 wt% O) in the resulting ceramic, with a consequent decrease of its high-temperature stability.^{213,254,255} γ-radiation or e-beam curing (usually performed in vacuum) allow to produce virtually oxygen-free ceramics, but the penetration depth typically limits the applicability of this method to

Table I. Techniques Applied to Preceramic Polymers (With or Without Fillers) to Manufacture a Shaped-Ceramic Component (Only Selected References are Listed)

Shaping technique	References
Casting/freeze casting	Melcher and colleagues ^{193–196}
Impregnation/infiltration	Satoa and colleagues ^{197–199}
Tape casting	Cromme <i>et al.</i> ²⁰⁰
Coating (spraying, dip- or spin-coating, chemical vapor deposition)	Goerke and colleagues ^{201–203}
Pressing (cold/warm—uniaxial, cold—isostatic)	Haug and colleagues ^{204–206}
Injection molding	Zhang and colleagues ^{207,208}
Extrusion	Mutsuddy and colleagues ^{209–211}
Fiber drawing	Bunsell and colleagues ^{212,213}
Blowing/foaming	Zeschky and colleagues ^{111,188,214}
Machining	da Rocha <i>et al.</i> ¹⁸⁵
Joining	Colombo and colleagues ^{186,215,216}
Rapid prototyping	Friedel <i>et al.</i> ²¹⁷
Ink jetting	Mott and colleagues ^{218,219}
Electro-hydrodynamic-spraying/spinning	Nangrejo and colleagues ^{220–224}
Aerosol spraying	Xiao and colleagues ^{225,226}
Self-assembly	Garcia and colleagues ^{227–229}
Microcomponent processing (UV/X-ray lithography, nano-/microcasting, replication, microextrusion, embossing/forging)	Hanemann and colleagues ^{230–240}
Microfluidics processing	Ye <i>et al.</i> ²⁴¹
Emulsion processing	Bakumov <i>et al.</i> ²⁴²
Formation of nanostructures (tubes, fibers, wires, cables, belts, coils), directly by pyrolysis	Otoishi and colleagues ^{190,195,243–249}

low-dimensional components such as fibers.^{256–258} However, direct foaming of siloxane pellets was achieved using e-beam.²²¹ Photo-sensitive functional groups can also be grafted onto the backbone of preceramic polymers to enable UV-curing, mainly for microcomponent or fiber fabrication.^{236,259,260} Curing at low temperatures (typically <200°C) using reactive gases such as ammonia, thionyl chloride, nitrogen dioxide, nitric oxide, halogenated or unsaturated hydrocarbon^{261,262} or reactive plasma, based on ammonia, methane, nitrogen, hydrogen, water, oxygen, silane, or borane gas,²⁶³ has also been proposed. Additionally, for selected precursors (for instance silicone resins containing Si–OH groups) it is possible to cure by immersing the shaped component in a highly alkaline solution.²¹¹

It has to be noted that, when a large amount of filler particles is added to the preceramic polymer, cross-linking might not be necessary, as the solid additives often offer sufficient support (limit the flow) to the polymeric matrix to retain the shape of the part upon heating. The introduction of fillers in fact heavily affects the rheology of the preceramic polymer.²⁶⁴

(2) Addition of Fillers

The polymer-to-ceramic conversion (see Panel B) occurs with gas release, (isotropic) volume shrinkage (20–30%, linear shrinkage) and formation of porosity (micro and macro). This typically leads to large defects, such as cracks or pores, which make the direct conversion of a preceramic part to a dense ceramic virtually unachievable, unless its dimension is typically below a few hundred micrometers (as in the case of fibers, coatings, or foams). It should, however, be noted that, very recently, a novel method for the fabrication of crack-free bulk bodies of PDCs has been proposed.²⁶⁵ A liquid preceramic polymer (e.g., a silazane) is infiltrated into a proprietary scaffold material, producing a polymer–matrix composite that can be machined using conventional equipment. Pyrolysis then yields a bulk ceramic of limited porosity content and without defects, because the scaffold material enables the release of the pyrolysis gases without any pressure build up.

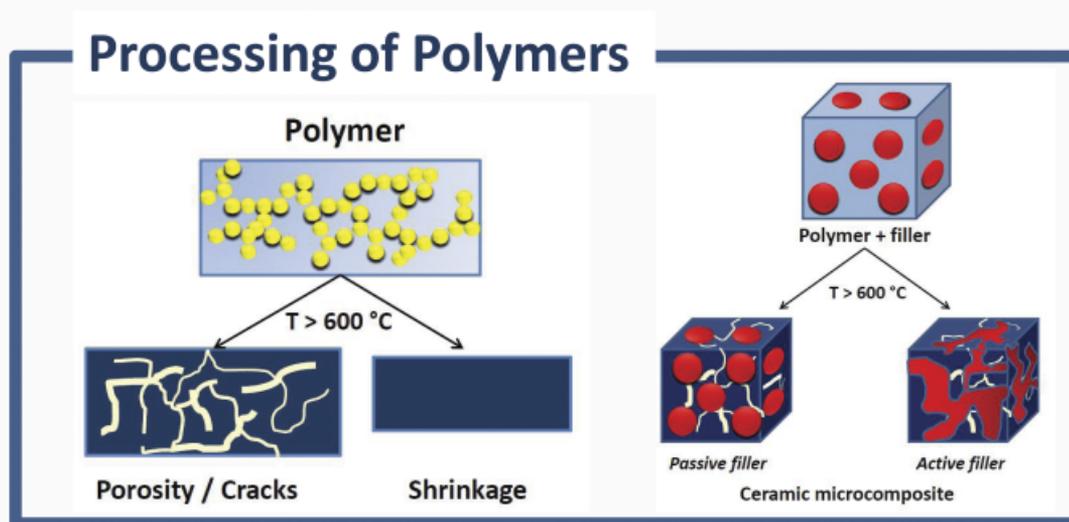
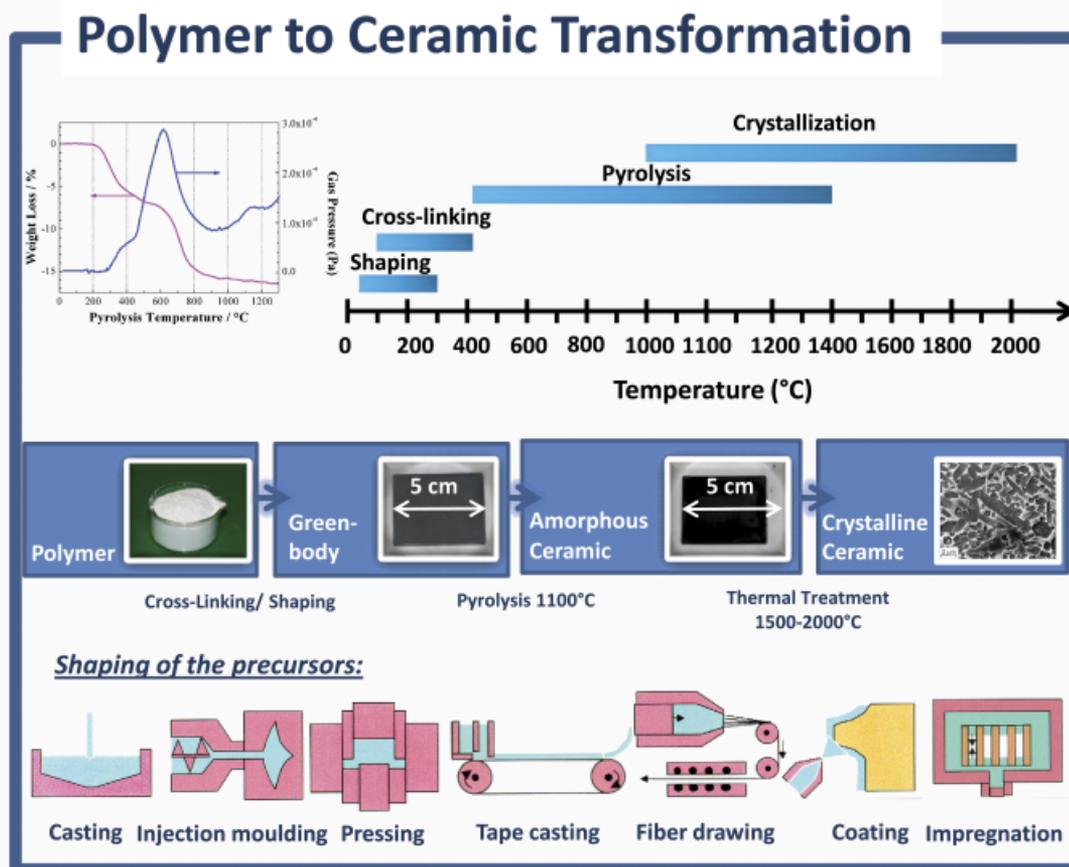
The introduction of fillers has been so far the main strategy followed enabling the fabrication of bulk components of size restricted only by the dimension of the pyrolysis furnace. Fillers of various nature (polymeric, metallic, ceramic) and shape/dimension (nano- or microsized powders, platelets, nanotubes,

nanofibers, chopped, or long fibers) can be added to a preceramic polymer before shaping. Fillers can serve multiple purposes and have several effects. First of all, they can be inert, that is they do not react at all, at any stage, with the preceramic polymer, its ceramic residue or the heating atmosphere. Typical examples are SiC or Si₃N₄ powders. In this case, they mainly serve the purpose of reducing the shrinkage of the component upon ceramization and eliminate the presence of macrodefects (cracks or large pores), by providing means of escape for the gases generated during pyrolysis.²⁶⁶ On the other hand, silazane mixed with silicon nitride powders leads, after hot pressing at high temperature, to micro/nanocomposites in which SiC nanoparticles are located both inter- and intra-granularly.²⁶⁷ The added ceramic powders can also constitute the majority of the volume of the final part, and therefore in this case the preceramic polymer merely acts as a low-loss binder allowing the achievement of higher densities in the final ceramic compared with conventional polymeric binders. Preceramic polymers have also been used as sintering additives for enhanced pressureless sintering of advanced ceramics such as silicon nitride²⁶⁸ or zirconium diboride.²⁶⁹ In some cases, the presence of a PDC as an intergranular phase also leads to improvements in some characteristics, such as high-temperature creep resistance, corrosion resistance, and mechanical properties, due to negligible grain growth occurring during high-temperature sintering.^{270,271} Moreover, it has been shown that growth of nanofibers (produced by the presence of a catalyst) from a preceramic polymer used as a binder can lead to porous components with a high specific surface area.¹⁹⁵ It should also be noted that when metallic powders are used, the use of a preceramic polymer as a reactive binder can afford useful properties to the metal components, such as increased wear or corrosion resistance.³⁰ Functional fillers such as molybdenum disilicide²⁷² or iron silicide²⁷³ can be added to modify certain properties, such as electrical conductivity or magnetic characteristics, and other fillers can be added to tailor the coefficient of thermal expansion of the ceramic component (for instance for coating on metals²⁷⁴ or sealing applications²¹⁶).

Metallic or intermetallic fillers have been termed “active,” as they react mainly with the gaseous products generated during the polymer-to-ceramic conversion, but also with the heating gas and/or the ceramic residue, generating carbides, nitrides, oxides, or silicides. A large volume of work has been devoted to the

Panel B. Polymer to Ceramic Transformation

1. Thermogravimetric analysis of a polymer decomposition and microstructural evolution with pyrolysis temperature;
2. Shaping of polymer-derived-ceramic components;
3. Processing and thermolysis of preceramic polymers containing fillers.



implementation of this processing concept to fabricate near-net-shape components, as the formation of ceramic compounds from metals occurs with volume expansion (up to 50 vol%), thereby reducing the shrinkage.^{275–277} It should nevertheless be noted that some residual porosity typically remains in the final part. However, large components with complex shapes can be produced at low processing temperatures (<1500°C), with properties that depend largely on the amount and type of fillers added and the degree of filler reaction achieved. Transition

metal carbides, such as NbC,²⁷⁸ Mo₂C,²⁷⁹ or WC²⁸⁰ for instance, can form during pyrolysis, greatly improving the hardness of the final ceramic part. Graphite powder can be added to siloxanes to exploit its carbothermal reduction reaction with the silica-based matrix, leading to the formation of SiC ceramics.²⁸¹

Oxide fillers can be inert or active, depending on the heating atmosphere, firing temperature, and their dimension. First of all, processing in inert atmosphere can lead to the formation of metallic particles, or silicides, carbides and nitrides, because of

reduction reactions with the carbon present in the preceramic polymer. For certain metals, it is actually advisable to utilize oxide powders rather than fine metallic particles, because they are not pyroforic and therefore safer to handle in air; after processing, the metal particles afford either magnetic or electrical characteristics to the ceramic. When processing in air to obtain oxide ceramics, α -alumina micrometer sized powder remains unreacted up to 1400°C. After mixing with a polysiloxane, it starts to transform into mullite at $T > 1500^\circ\text{C}$.²⁸² However, if nanosized γ -alumina powder is used, the reaction with the siloxane-derived silica matrix occurs at temperatures as low as 1250°C, leading to a single-phase mullite ceramic at 1350°C, with crystal grains about 300 nm in size.²⁸³ Other ceramic compositions can be produced by this approach, such as SiAlON,²⁸⁴ wollastonite,²⁸⁵ and cordierite, with a high degree of microstructural control on the resulting crystalline phase assemblage (lack of additional, spurious phases). Organically functionalized clay has also been used as a nanosized reactive filler, although the burn out of the organics during heating hindered the formation of a dense ceramic. Carbon nanofibers and nanotubes have also been added to preceramic polymers with the aim of modifying electrical and/or mechanical properties.^{286,287} In this case, the possibility of processing the preceramic precursor in a molten state or in solution generally enables to obtain a good dispersion of the fillers throughout the ceramic matrix.²⁸⁸

Polymeric fillers can also be added to preceramic polymers; in this case, they decompose completely upon pyrolysis and therefore they act as sacrificial fillers, leading to the formation of porosity whose size and amount depend on the characteristics of the filler itself. A particularly interesting approach to creating a large volume of porosity is to combine expandable polymeric microbeads with siloxanes²⁸⁹; upon heating to temperatures below 150°C, the microbeads undergo a four- to eightfold volume expansion within the molten silicone resin matrix. This limits the amount of organics to be burned out during pyrolysis, with advantages in terms of reduction of noxious gases and of occasional formation of cracks.

(3) Polymer-to-Ceramic Conversion

The thermal decomposition behavior of basic organosilicon polymers $-\text{[SiR}^1\text{R}^2\text{-X]}_n-$ is presented in Fig. 6. Starting from different classes of silicon-based polymers such as poly(organocarbosilanes) (where $\text{X} = -\text{C}(\text{R}^3\text{R}^4)-$), poly(organosiloxanes) (where $\text{X} = -\text{O}-$), poly(organosilazanes) (where $\text{X} = \text{NR}^3$) and poly(organosilylcarbodiimides) (where $\text{X} = -\text{N}=\text{C}=\text{N}-$), after the thermal treatment at about 1000°C, amorphous SiC, $\text{Si}_x\text{C}_y\text{O}_z$, and $\text{Si}_x\text{C}_y\text{N}_z$ PDCs can be obtained, and the ratio Si/X can be varied. By using defined organic substituents (R^1 and R^2) at silicon, the ratio Si/C can be controlled as well.

For the quantitative analysis and detailed study of the decomposition behavior of preceramic polymers as well as for optimization of the polymer-to-ceramic transformation, thermal gravimetric analysis (TGA) is the method of choice. *In situ* investigation of volatile species and fragments of the decomposition products can be performed by coupling the TGA with a mass or FTIR spectrometer. Some characteristic examples of TGA investigations of different types of Si-polymers (polysilazanes and polyborosilazanes) are given in Fig. 7.

After shaping and cross-linking, the preceramic part has to be converted into a ceramic. The details of the polymer-to-ceramic transformation are illustrated in Panel B. This conversion leads to the decomposition or elimination of organic moieties (such as methyl, phenyl, vinyl groups) and Si-H, Si-OH, or Si-NH_x groups. Thermal or nonthermal processes can be applied (see Table II). Naturally, the most widely used is oven pyrolysis, in which the flowing gas continuously removes the decomposition gases from the system.¹³³

Hot pressing²⁹⁰⁻²⁹² and spark plasma sintering^{293,294} have been applied for consolidation of already pyrolyzed powders rather than as ceramization methods, as the gas release during processing of unpyrolyzed powders could damage the mold. Chemical vapor deposition²⁹⁵ and plasma spraying²⁹⁶ have been used for the direct deposition of preceramic polymers (mainly oligomers) on various substrates to produce ceramic coatings. The ceramization occurs because of the temperature of the plasma, which decomposes the precursors, or because the substrate is heated. Rapid thermal annealing of silicones leads to the formation of coatings to be used as protective and dielectric layers on electronic devices²⁹⁷; it is typically performed in air, and therefore leads to the formation of silica. Laser pyrolysis has been used to ceramize preceramic coatings, and has the additional advantage of the capability for selective writing.²⁹⁸ However, the laser radiation has to be carefully tuned in order to avoid damage to the substrate, and the polymer has to be able to absorb such radiation. Carbon inclusions or surface coatings have been successfully used for this purpose. The use of pulsed laser allows the minimization of the volume irradiated, leading to self-standing three-dimensional components with high aspect ratio after several repetitive passes on a liquid precursor bath.²⁹⁹ Laser pyrolysis has also been applied to the production of nanosized powders by direct irradiation of an aerosol.³⁰⁰ When high pressure is added, as for example by using a diamond anvil cell, novel ceramic materials such as CN-based compounds or spinel-type silicon, zirconium, or hafnium nitrides can be synthesized, with interesting structural, mechanical, and functional properties.³⁰¹ Microwave pyrolysis has been rarely used in conjunction with preceramic polymers, probably because pure polymers do not absorb the microwave radiation, and therefore either hybrid

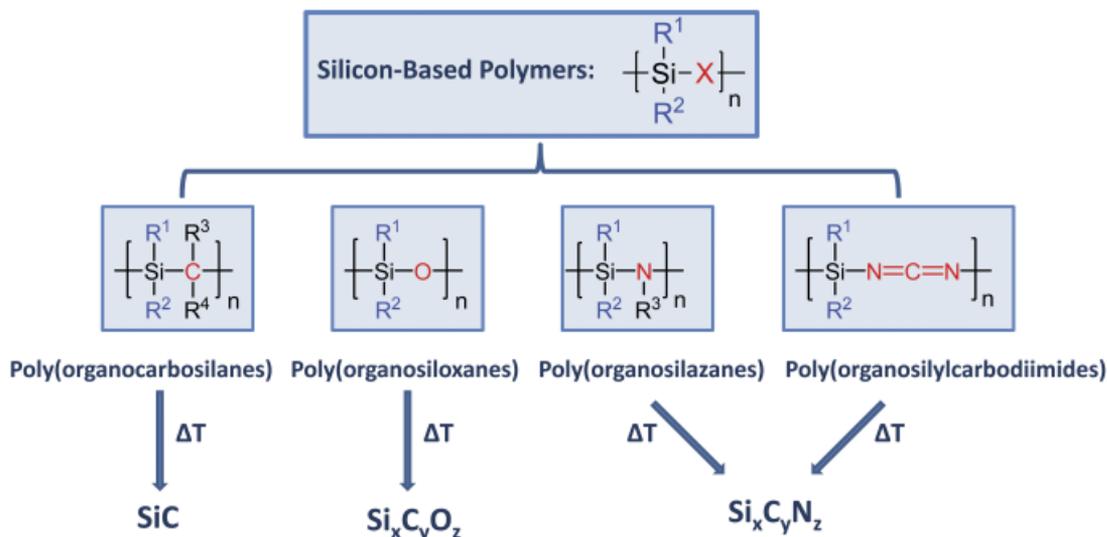


Fig. 6. Thermal decomposition of silicon-based polymers (oversimplified representation of the molecular structure of the precursors).

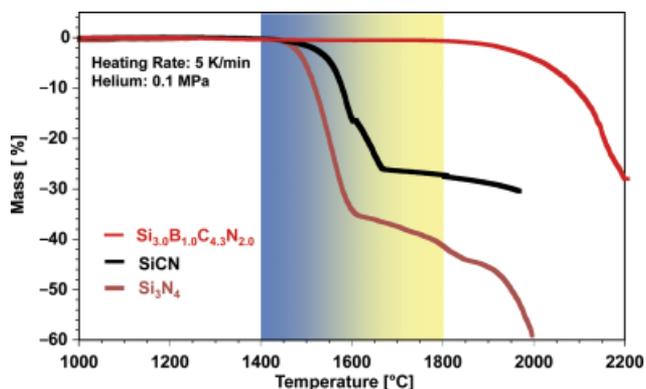


Fig. 7. Thermal gravimetric measurements of SiBCN ceramic compared with SiCN and Si₃N₄ up to 2200°C.

microwave heating or susceptor fillers (such as SiC or C) have been used.³⁰² It would, however, be very interesting to evaluate the effect that such a different thermolysis method could have on characteristics such as the ceramic yield and the crystalline phase assemblage of the resulting pyrolyzed component. Ion irradiation is a nonthermal process that has been applied to preceramic layers; ceramization occurs via elimination of hydrogen atoms via cleavage of C–H bonds, and part of the residual carbon is converted to diamond-like carbon clusters, which afford luminescence and high hardness to the coatings.^{303–305} Irradiation has also been used to produce nanowires, after dissolution of the noncross-linked areas of a preceramic polymer coating.³⁰⁶

(4) Processing Parameters Influencing the Fabrication of PDCs

The ceramization of preceramic polymers is a complex, yet extremely versatile approach to the formation of ceramic components. Several experimental parameters can be manipulated to tailor the outcome of the process, and this represents a great challenge as well as an opportunity. Table III lists the main factors which affect fundamental PDC characteristics such as composition, microstructure, density, ceramic yield, shape, surface finish, and flaw population, and therefore their properties and applications.

The precursor properties obviously influence its capability of being processed, and therefore the shaping method has to be adapted to the individual characteristics of the preceramic material. For instance, polymers such as silazanes or carbosilanes which are sensitive toward ambient humidity and tend to react by incorporating oxygen, have to be handled accordingly, even though in some cases warm pressing can be used without intro-

Table III. Parameters that Play an Important Role in the Processing of Preceramic Polymers (Only Selected References are Listed)

Processing parameters	References
Characteristics of the precursor (rheology, ceramic yield, reactivity, cross-linking)	Kroke and colleagues ^{121,307}
Presence and type (active, inert, functional) of fillers	Greil and colleagues ^{275–277}
Shape of fillers (whiskers, platelets, nanotubes, short fibers, powders)	Shibuya <i>et al.</i> ²⁸⁶
Dimension of fillers (micro- or nanometer)	Griggio <i>et al.</i> ²⁸³
Atmosphere type (inert/reactive/vacuum)—during shaping or during ceramization	Greil and colleagues ^{276,308–310}
Atmosphere pressure—during ceramization	Liew and colleagues ^{290–294}
Heating rate	Colombo <i>et al.</i> ¹
Heating temperature	Colombo <i>et al.</i> ¹
Dwelling time	Colombo <i>et al.</i> ¹

ducing significant contaminations.^{121,307} The degree of (partial) cross-linking of preceramic polymers can significantly affect their plastic forming capability, leading to hindered flow at processing temperature and formation of residual porosity.^{204,311} The shape of the fillers (especially those with high aspect ratio) can reduce the isotropy in the shrinkage during ceramization, leading to deformed components.²⁸⁶ Their dimension influences their reactivity toward the surrounding matrix,²⁸⁴ and this can be a concern for instance with metal powders (which typically are of several microns in diameter) because it could leave some unreacted material at the core of the filler particle.³⁰⁸ The type of atmosphere can modify the composition of the resulting ceramic, even when active fillers are not present³⁰⁹; the oxygen content in the inert gas is of particular importance when processing thin films, as it can lead to the unwanted elimination of carbon-containing moieties in the material.³¹⁰ The gas pressure also has a strong effect: for instance, vacuum promotes carbothermal reduction reactions and can therefore promote crystallization. Added pressure (either mechanical—hot pressing, or gaseous—hot isostatic pressing) has been shown to hinder the carbothermal reduction reactions occurring at high temperature, with formation of SiC (from reaction with the silica or the silicon nitride species present), leading to a suppression of crystallization.^{291,294} Also, there is experimental evidence that using high nitrogen gas pressures (up to 200 atm) leads to the incorporation of some nitrogen into the final ceramic, resulting in modified properties (for instance electrical conductivity²⁹⁰). The heating rate affects the ceramic yield (oligomers can be released, with a decrease in the ceramic yield, if insufficient time for cross-linking during heating is given) but also the composition. For instance, the very fast energy transfer that occurs with laser heating enables the processing of thin layers in air, avoiding the introduction of oxygen contamination.²⁹⁸ Temperature-related processing parameters such as heating rate and dwelling temperature and time influence the composition and microstructure of the ceramic, as they affect the extent of crystallization, carbothermal reduction reactions, and filler reactions occurring in the material. The heating rate also affects the formation of cracks due to gas release, consequently in parts above a certain size (a few mm³) it has to be kept rather low (e.g., ~2°C/min or less), at least within the polymer-to-ceramic transformation temperature region.

Finally, it is noteworthy that for some applications it is actually not necessary to carry the polymer-to-ceramic transition to completion, for instance, if a large amount of micro- and meso-porosity is desired³¹² or if net-shape processing is required,

Table II. Ceramization/Consolidation Techniques Applied to Preceramic Polymers (Only Selected References are Listed)

Ceramization/consolidation methods	References
Oven pyrolysis	Blum <i>et al.</i> ¹³³
Hot isostatic pressing	Liew <i>et al.</i> ²⁹⁰
Hot uniaxial pressing	Breval and colleagues ^{291,292}
Spark plasma sintering	Wan and colleagues ^{293,294}
Chemical vapor deposition	Bouyer <i>et al.</i> ²⁹⁵
Plasma spraying	Krüger and Raymond ²⁹⁶
Radiation pyrolysis (rapid thermal annealing)	Chandra and Martin ²⁹⁷
Laser pyrolysis	Colombo and colleagues ^{298–300}
Laser pyrolysis + high pressure (diamond anvil cell)	Dzivenko <i>et al.</i> ³⁰¹
Microwave pyrolysis	Danko <i>et al.</i> ³⁰²
Ion irradiation	Pivin and colleagues ^{303–306}

to manufacture complex parts without final machining.³⁰⁷ Also, luminescence can be developed when processing at these intermediate temperatures.³¹³ Furthermore, preceramic polymers not subjected to ceramization can be used to produce components which display improved properties (e.g., higher thermal and solvent resistance) over conventional polymers, as in case of microreactors³¹⁴ or antigriffiti coatings.^{315,316}

IV. Microstructure of PDCs

PDCs are intrinsically complex systems, which undergo profound microstructural changes when exposed to temperatures > 1000°C. Several studies have shown that the high-temperature properties such as the resistance to crystallization and to thermal degradation depend to a great extent on the microstructure of the amorphous phase of the ceramics. One of the most intriguing characteristics of PDCs is the presence of nanodomains in the microstructure that persist up to very high temperatures. It was proposed that the nature of the nanodomains is the basis for the remarkable resistance of PDCs to crystallization even at ultrahigh temperatures.²³ Reports in the literature confirm that SiCN contains nanodomains with 1–3 nm in size.^{317–319} Recent analysis of experimental small-angle X-ray and neutron scattering (SAXS) data allows the identification of the type, composition and shape of these nanodomains in carbon-rich SiCN ceramics.³²⁰

PDCs can be amorphous up to 1000°–1800°C, mainly depending on the molecular structure and composition of the precursor used. At elevated temperatures, the devitrification process of the initial amorphous network starts and leads to local crystallization of different phases. The redistribution of the chemical bonding results in phase separation and finally it leads to nucleation and growth of nanocrystals. Moreover, in many cases decomposition is followed by phase separation and crystallization with the releasing of gaseous products such as CO, SiO, or N₂ and others.

Regarding the microstructural evolution of PDCs from the amorphous state to the partially crystalline state, the following major aspects can be highlighted: (i) during annealing, the entire bulk of the material undergoes a phase separation process; (ii) separation of a “free” carbon phase is subjected to a graphitization process; (iii) with increasing temperature, the local formation of nanocrystals occurs. The “free” carbon is defined with respect to stoichiometry as the amount of carbon not bonded to silicon in ceramic.

There are several techniques that have been applied to the characterization of the microstructure in PDCs. The methods can be classified into techniques which provide average or integral information such as MAS–NMR, XRD, HE–XRD, SAXS, SANS, FTIR, and Raman spectroscopy and techniques which give information about local properties at the nanometer scale such as TEM, SEM, EELS, and EF-TEM. Moreover, theoretical studies have been conducted in order to explain the unusual microstructural features of PDCs as well as the crystallization behavior of the systems and the fate of carbon during the thermal decomposition.

Typical structural features of PDCs based on SiCN and SiCO are listed in Table IV. In the discussed cases, the amorphous phases are formed in carbon-rich regimes, relative to the stoichiometric mixtures of the crystalline forms. A key question in understanding the transformation of the polymeric state to a nanostructured ceramic is the role played by the “free” carbon.

The introduction of further elements (such as boron or aluminum) into the preceramic polymers can increase the high-temperature stability, creep, and oxidation resistance, which are features directly correlated to the nanostructure of the ceramics. These mechanical and chemical as well as other functional properties of PDCs are characteristic of the “amorphous” state, which can persist at temperatures as high as 1800°C.

(1) Raman Spectroscopy

A main feature of PDCs is their possibility to incorporate “free” carbon into the microstructure. Raman spectroscopy suggests the existence of graphene sheets of carbon with some degree of long-range order; unfortunately, in the amorphous state, the bands are overlapped and their characteristics can be determined only if coupled with molecular simulations. Raman spectroscopy is intrinsically a “local” method because the laser beam is focused on areas of only a few micrometers of the sample. Nevertheless, the local variations in compositions or phase content mostly occur on the nanometer scale and Raman data are acquired with the lateral resolution of a few micrometers, giving an average signal over that specimen volume.

Furthermore, Raman spectroscopy is an important nondestructive tool for the examination of the structural evolution of the “free” carbon phase in PDCs.^{328–333} The major features of “free” carbon in the Raman spectra of PDCs are the so-called disorder-induced “D- and D’ bands” at approximately 1350 and 1620 cm⁻¹, the “G band” at approx. 1582 cm⁻¹ due to in-plane bond stretching of *sp*² carbon, as well as the G’-band (the overtone of the D-band which is always observed in defect-free samples at 2700 cm⁻¹) (Fig. 8).^{329–333} Another Raman feature at about 2950 cm⁻¹, associated with a D+G combination mode and induced by disorder, is observed in the spectrum of carbon as well.

Furthermore, the nanoscaled “free” carbon clusters play a significant role in tuning the properties of PDCs. Therefore, a quantitative measuring of their concentration is needed. Very recently, Jiang *et al.*³³⁴ published a simple Raman-spectroscopy-based quantitative method to measure the “free” carbon concentration in SiCN ceramics by using silicon as an external reference (see Figs. 9(a)–(c)).

The volume ratio of silicon to SiCN (V_{Si}/V_{SiCN}) exhibits a linear relationship with the normalized intensity ratio (I_{Si}/I_{CK}) and the slope of the curve represents the “free” carbon concentration in SiCN (Fig. 9(c)). For the same system, measuring the diameter of the carbon clusters L_a from 80 measurements, an average size of 24 ± 2 Å was determined (Fig. 9(d)).

(2) Multinuclear MAS–NMR

The multinuclear MAS–NMR is one of the most accurate average techniques for the study of the type of coordination of NMR sensitive elements in amorphous and crystalline PDCs.

Table IV. A Summary of the Structural Characteristics of Polymer-Derived SiCN and SiCO Ceramics

Atomic and nanostructure	SiCN	Technique	SiCO	Technique
Si Atoms	Tetrahedrally bonded to C and N	NMR ^{321,322} SAXS ³²³	Tetrahedrally bonded to C and O	NMR ^{324,325}
C Atoms	- <i>sp</i> ³ When bonded to Si - <i>sp</i> ² When bonded to other C atoms -Not bonded to N	NMR ^{321,322}	→ <i>sp</i> ³ When bonded to Si → <i>sp</i> ² When bonded to other C atoms	NMR ^{324,325}
Size of Nanodomains	1–3 nm gradually increasing in size with annealing	SAXS and SANS ³²⁶	1–3 nm in size revealed by etching in dilute HF	SAXS ³²⁷

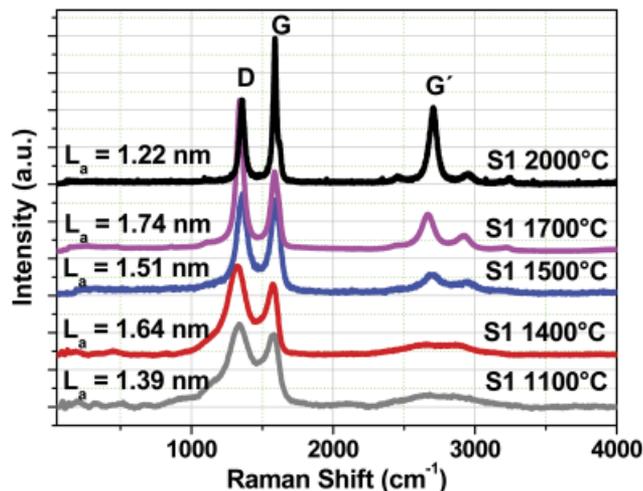


Fig. 8. Example of the carbon-phase evolution during thermal annealing of a polymer-derived carbon-rich SiCN ceramic.¹⁸²

Indeed, the phase-separation process in PDCs was originally discovered by means of NMR.

In the case of polysilazanes and polysilylcarbodiimides, ²⁹Si MAS-NMR measurements have shown that the resulting amorphous SiCN ceramics have a completely different microstructure (Fig. 10). Polysilazanes yield a single-phase amorphous SiC_xN_y (x+y = 4) phase, where Si is bonded to C and N, as shown in Fig. 10, while polysilylcarbodiimides form a two-phase amorphous system composed predominantly of amorphous Si₃N₄ clusters and C clusters.²² The formation of the particular amorphous structures in polysilylcarbodiimide-derived SiCN ceramics retards the crystallization and phase-partitioning processes that lead to the thermodynamically stable crystalline Si₃N₄ and SiC phases. Solid-state NMR studies clearly revealed that amorphous Si-C-N phases obtained from polysilylcarbodiimides form crystalline SiC around 1600°C, while the corresponding silazane-derived materials with an analogous C/Si ratio start to crystallize about 50–100°C lower.¹⁵⁶ The characteristic nanodomain microstructures are schematically represented in Fig. 10.^{22,156,182}

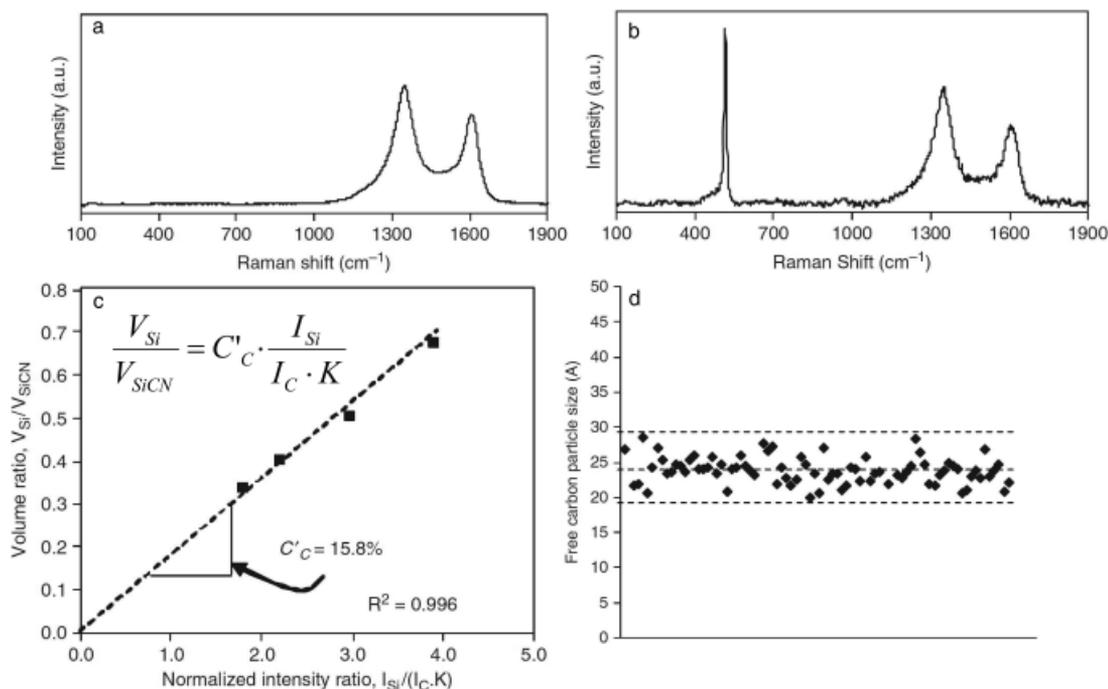


Fig. 9. Raman spectra of SiCN powder synthesized at 1300°C (a) and of the Si-SiCN mixture with a volume ratio of 1:1 (b). (c) Plot of the Si to SiCN volume ratio as a function of the normalized Si to SiCN Raman intensity ratio. (d) “Free” carbon sizes measured in SiCN polymer-derived ceramics.³³⁴

Recently, a more detailed microstructural model was proposed for polysilylcarbodiimide-derived ceramics. In the case of carbon-rich polysilylcarbodiimides,¹⁸² the thermal decomposition at temperatures up to 1100°C yields a SiCN ceramic containing three amorphous phases composed of Si₃N₄, C, and dispersed SiC domains. The model (Fig. 11) was confirmed by elemental analysis,³³⁵ electrical conductivity,³³⁶ and recently by SAXS analysis.³²⁰

Several studies have shown that the insertion of boron at the molecular level can improve the high-temperature stability, oxidation resistance, and high-temperature mechanical properties of PDCs. In the case of SiBCN ceramics, solid-state NMR investigations on as-pyrolyzed and annealed SiBCN ceramics revealed that the boron environment depends on the Si/B ratio and is quite different in the individual native preceramic polymer. In contrast, the coordination sphere of boron resembles that of a mixture of BN₂C and BN₃ sites for the samples heat treated at 1000°C independent of the starting Si/B ratio. At the same time, the number of aliphatic carbons that make the interconnection between the silicon and the boron atoms decreases. This evolution suggests the preferential cleavage of B-C bonds with the evolution of methane and ethane while nitrogen atoms bonded to silicon sites migrate to boron during the polymer-to-ceramic conversion as confirmed by the appearance of NB₃ sites. Moreover, deprotonation of the nitrogen sites leads to the formation of C-N-X (X = Si or B) structural units and a distribution of SiN_xC_{4-x} (1 ≤ x ≤ 4) sites is observed. These findings suggest that boron atoms are homogeneously dispersed in the silicon carbonitride phase supporting the high thermal stability analyzed in these compounds.³³⁷

(3) X-Ray Diffractometry (XRD)

In the materials that contain a rather high volume fraction of crystalline phase, XRD is a powerful and quick method for the determination of the crystallite sizes of the different phases and their polymorphs in PDCs. By means of Rietveld refinement of the XRD patterns using the approximation of different shapes of the particles, the cluster sizes of α- and β-SiC, SiO₂ and Si₃N₄ phases can be determined. The XRD analysis has a detection limit of 1–2 vol%, therefore the identification of the first nanocrystals starting to grow in the amorphous bulk material by XRD is not possible.

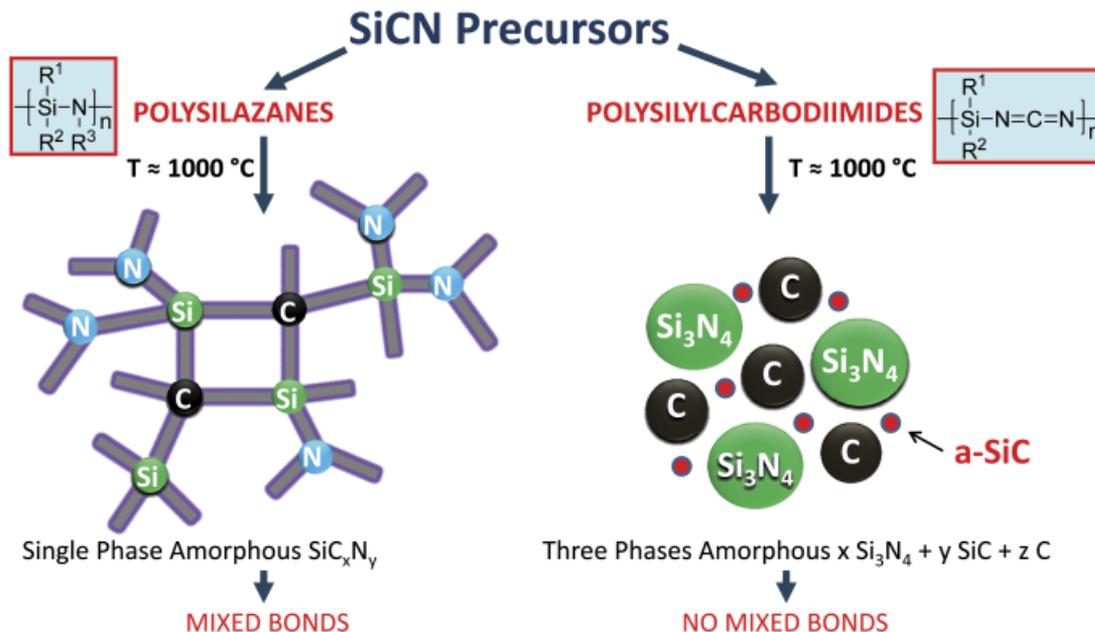


Fig. 10. Microstructure of amorphous SiCN ceramics derived from polysilazanes and from polysilylcarbodiimides.

Furthermore, regarding the formation of crystalline carbon in PDCs at very high temperatures, XRD results provide the opportunity to determine two important parameters for the characterization of the carbon phase. By means of XRD analysis, the in-plane crystallite size L_a and the crystallite thickness L_c or stacking for all types of carbon phases can be derived as well.³³⁸

(4) TEM

Intensive electron microscopic studies have been conducted on PDCs, showing the first stages of local crystallization and identifying nanocrystalline phases after initiation of the devitrification process of amorphous PDCs. In the amorphous state TEM has shown that PDCs are generally featureless. However, the presence of nanosized turbostratic or graphitic carbon was identified in many cases.

In particular, the microstructural evolution of silicon oxycarbide (SiCO) and silicon carbonitride (SiCN) ceramics has been studied for many years. Such PDCs are typically amorphous up to rather high temperatures, but they nevertheless provide very intriguing ceramic-like properties, such as good creep and oxidation resistance.^{6,24,293,339,340} TEM imaging reveals no major variation among different samples synthesized from one specific precursor. Using electron diffraction mode in TEM, the samples show fine differences in the short-range order depending on the composition and annealing temperature as depicted for the SiCN system³⁴¹ in Fig. 12.

Generally, excess carbon beyond the stoichiometric amount necessary to saturate all Si valences is present in many PDC systems. At lower temperatures, the carbon remains homogeneously dispersed in the amorphous material (solid solution like). Above 1000°C , the carbon forms either so-called basic-

structural units (see Fig. 13)³⁴² or locally enriched regions of turbostratic graphite. Although the exact nature of this excess “free” carbon is not well studied for the different PDC systems, several reports have attributed the exceptional properties of these amorphous polymer-derived materials, such as high chemical durability in aggressive media and their resistance to crystallization, to the presence of this “free” carbon phase and its distribution within the amorphous network.^{47,121,186,304,343–352}

After annealing a SiCO ceramic at 1000° and 1200°C the atomic distribution is still completely homogeneous. At higher temperatures (1450°C) (Fig. 14) the carbon dispersion becomes rather inhomogeneous on the nanometer-scale. In the case of carbon-rich SiCO ceramics and on the basis of TEM studies, the “nanostructural picture” of these materials can be described as a percolation network of carbon encapsulating SiO_2 domains, in addition to local precipitation of SiC due to local carbothermal reduction.

(5) EELS

The EELS technique allows the detection of variations within the local coordination of Si (L-edge) and C (K-edge) atoms upon different heat treatments in Si-based ceramics. Because of the different energies of Si–C, Si–N, and Si–O bonds, the threshold energy of the Si L-edge varies as the atomic species coordinating the silicon atom change. The analysis of the carbon K-edge allows to monitor the structural evolution of the “free” carbon phase, having two main features π^* and σ^* at 285 and 292 eV, respectively, corresponding to sp^2 C and sp^3 C.

(6) Electron Diffraction Technique

The electron diffraction method uses the same principle as XRD and it is measured during the TEM analysis in order to identify the crystal structure of micro- and nanosized crystals. When this method is used in combination with an imaging plate, which provides a linear contrast response to the incident diffracted beam, the investigations of the local short-range order in amorphous materials can be performed.

(7) SAXS

SAXS analysis provides detailed information regarding the size distribution of the domains and the crystallites but cannot distinguish between the chemistry and the structure of the domains. Complementary to the NMR results, SANS, and SAXS data

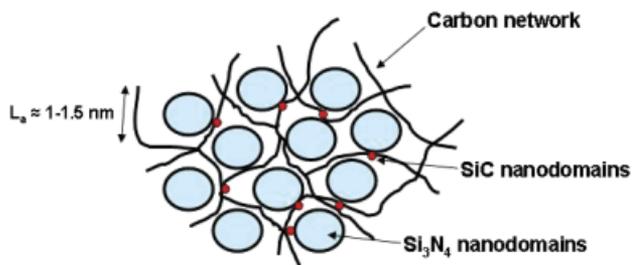


Fig. 11. Microstructural model for polysilylcarbodiimide-derived ceramics.³³⁵

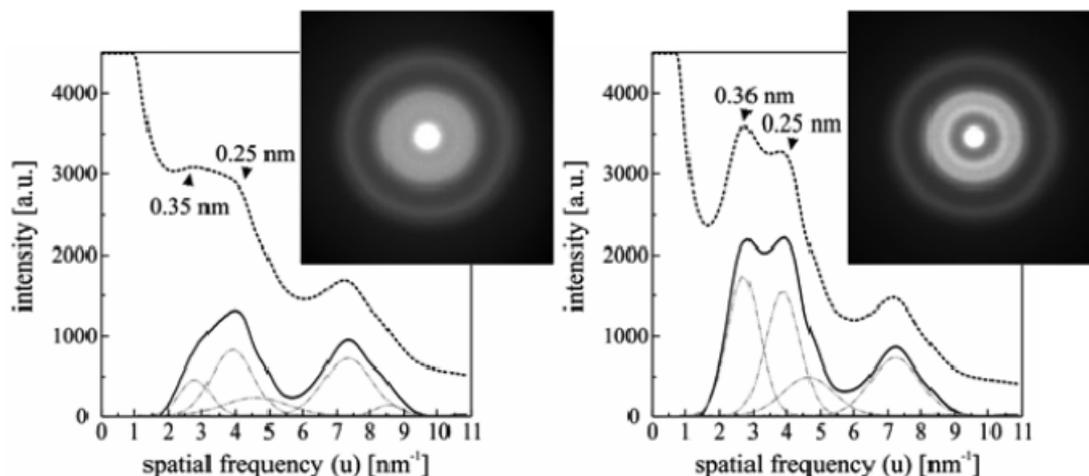


Fig. 12. Electron diffraction patterns and corresponding line scans of two SiCN materials annealed at 1400°C. The two samples, although predominantly amorphous, reveal a different glass network structure. However, the details of the nanostructure of such materials are not provided by this analysis.³⁴¹

proved that phase separation is accompanied by an improvement of the local short-range order.

In 2005, Saha *et al.*³²⁸ reported the characterization of nanodomains and nanocrystals for SiCN and SiCN–ZrO₂ PDCs by a combination of methods such as Bragg diffraction, SAXS, and TEM. One year after, the same authors proposed a simple geometrical model based on surface-to-volume ratio of the domains which was moderately successful in predicting the domain size in silicon-oxycarbides (see Fig. 15).³⁵³

The principal assumptions in this model are based on the framework of the amorphous structure justified on the basis of NMR data and on the creep and viscoelastic behavior of the SiCO ceramic at temperatures beyond 1000°C. The model has only one adjustable parameter, which defines the composition of the layer of the mixed bonds that are assumed to surround the silica domains. Reasonable values of this parameter give good agreement with the experiment. The derived concept has several approximations and limitations; one of them is related to the

carbon content: when the carbon content is increased the domain size appears to reach a lower limit of ca. 1 nm (compositional limit). The domain structure is highly stochastic, as clearly deducible from the SAXS data, and therefore, the convergence of experimental and theoretical values may be coincidental. Shortly after this report, it was shown that amorphous SiCO ceramics can be etched with hydrofluoric acid leaving behind a porous structure with a median pore diameter of approximately 3 nm. The change in the composition after etching shows that only silica (not carbon) is removed by etching.³⁵⁴ All these findings concerned only SiCO ceramics with low to moderate carbon concentration.

Very recently, several carbon-rich SiCN ceramics have been investigated by means of SAXS spectroscopy.³²⁰ The nanostructure of novel carbon-rich silicon carbonitride (SiCN) ceramics synthesized via thermolysis of poly(methylphenylsilylcarbodiimide), $-\text{[Ph(CH}_3\text{)Si-NCN]}_n-$, at 1300°, 1500°, 1700°, and 2000°C was investigated and the structural information obtained from several experimental methods was combined together with theoretical modeling of the SAXS data to obtain a detailed model of the temperature-dependent evolution of nanodomains comprising of “free” carbon, SiC, and Si₃N₄ in SiCN-based ceramics. For the first time, information on size, composition, shape, orientation, and volume fraction of the nanodomains was provided by extensive modeling of the experimentally SAXS-derived data. The results clearly show that

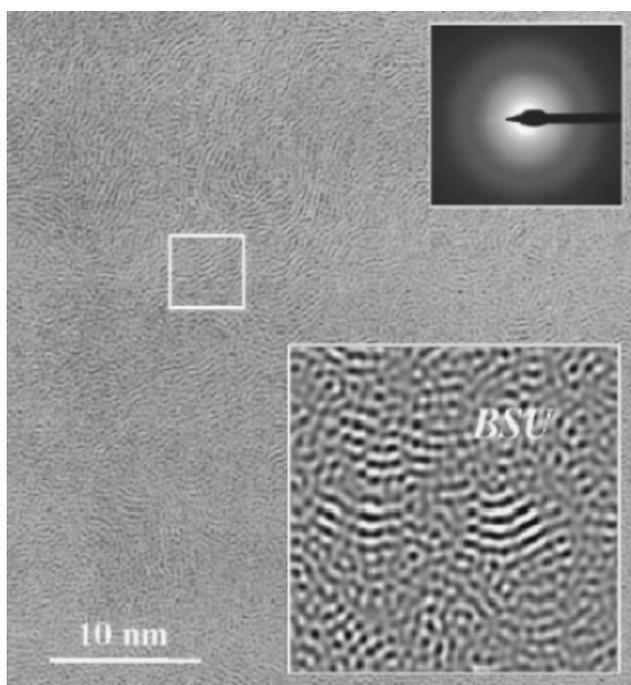


Fig. 13. High-resolution TEM image of a SiCO ceramic sample synthesized at 1200°C. The overall matrix is amorphous (SAD inset on right upper corner), however, small basic structural units (BSU), as shown in the lower inset, are homogeneously distributed throughout the amorphous matrix.

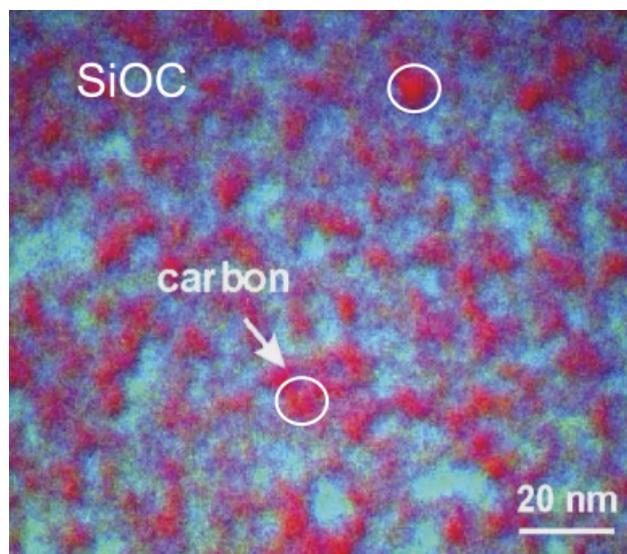


Fig. 14. EF-TEM image of a carbon-rich SiCO ceramic annealed at 1450°C. The local enrichment of the “free” carbon phase is noticeable (red regions, circled).⁴⁷

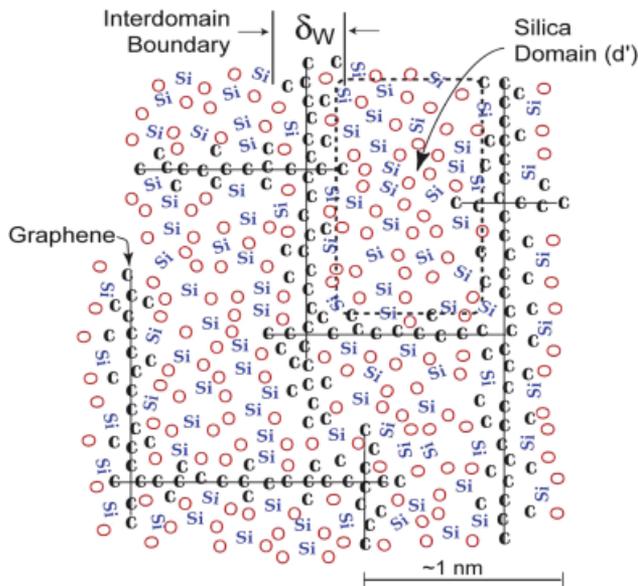


Fig. 15. Proposed model for the nanodomain structures in polymer-derived SiCO.³⁵³ The interdomain boundary consists of graphene layers with mixed Si-C-O bonds forming the interface between silica and carbon domains.

excess carbon in the SiCN composition plays an important role in the temperature-dependent formation of the nanodomain structure of polymer-derived SiCN ceramics (Fig. 16).³²⁰

(8) Theoretical Modeling

Because of the restrictions of many characterization methods with respect to the investigation of amorphous ceramic systems, a significant emphasis was placed on computational methods to elucidate the structure of this kind of disordered matter. Modeling and simulations of amorphous materials thus can greatly enhance the experimental resolution and provide new insights into the structure of amorphous materials.

Several theoretical papers^{323,356,357} have already reported on the microstructure of amorphous precursor-derived Si-C-N ceramics. In the first paper, Dürr *et al.*³²³ exploited experimental information from neutron and X-ray scattering data in order to investigate the atomic structure of the amorphous ceramic through a Reverse Monte Carlo calculation. The work of Matsunaga *et al.*³⁵⁶ is based on classical MD simulations using the empirical Tersoff potential, while Amkreutz *et al.*^{357,358} performed *ab initio* MD simulations within a density-functional-based tight-binding scheme. The latter approach, where the atomic forces are calculated on a quantum mechanical basis, is very accurate but has severe size (≈ 100 atoms) and time (≈ 1 ps) limitations.

Moreover, Resta *et al.*^{355,359} have performed classical MD simulations of Si-C-N ceramics in the nanometer/nanosecond scales, modeling the atomic interaction by the Tersoff³⁶⁰ potential. The theoretical approach of Resta *et al.*^{355,359} is within the same theoretical framework as the one of Matsunaga *et al.*,³⁵⁶ but much wider in scope and with improved statistics. Resta's work considers a more varied range of compositions, larger samples, and longer, by three orders of magnitude, simulation times. The separation of C domains in the SiCN system was investigated in an amorphous SiCN system (Fig. 17(a)) and in a partially crystalline sample (Fig. 17(b)).³⁵⁵

In 2005, Golczewski and Aldinger³⁶² reported on a thermodynamic model developed to rationalize the enhanced persistence of amorphous Si-C-N ceramics. In the same year, Kroll³⁶³ published model structures of some PDCs, including amorphous Si-C-N, which has been simulated by *ab initio* molecular dynamics.

Kroll^{363,364} have extended a traditional approach of modeling amorphous silicon and developed an algorithm to provide ran-

dom network structures with well-defined chemical order in multicomponent systems. A target of this work was to control the degree of disorder in a model structure to study segregations and the onset of crystallization in such materials and the evolution of "free" carbon phase during thermal decomposition in SiCO³⁶⁵ and SiCN systems (Fig. 18).¹

V. Properties of PDCs

(1) Electrical Properties

Electrical properties of PDCs have been measured and reported by Yajima³⁰ since the early discovery of these new materials. Yajima studied the resistivity of polycarbosilane-derived SiC as a function of pyrolysis temperature and also suggested a possible application to fabricate small-size igniters. In the late 1980s Mackenzie's group at UCLA reported the electrical characterization of polycarbosilane-derived SiC thin films, their semiconducting behavior and also demonstrated the possibility of B and P doping and the fabrication of P-N heterojunctions.³⁶⁸⁻³⁷⁰ Surprisingly, the study of electrical properties of PDC was neglected for almost one decade, and was undertaken again in Germany only in 1999, with the work at Bosch³⁷¹ and in 2000 with the work of Greil's group.³⁷² At present, the literature on electrical properties of PDCs covers the Si-C-N³⁷³⁻³⁷⁶ as well as the Si-C-O³⁷² systems.

The room-temperature dc conductivity of PDCs, σ_{dc} , varies up to 15 orders of magnitude (typically in the range 10^{-10} – 10^{-8} to 1 ($\Omega \cdot \text{cm}$)⁻¹) depending on the polymeric precursor, composition, pyrolysis temperature, and atmosphere. For low pyrolysis temperature, i.e. $T_{\text{pyrolysis}} \sim < 600^\circ\text{C}$ PDCs can be better described as insulators with $\sigma_{dc} < 10^{-10}$ ($\Omega \cdot \text{cm}$)⁻¹. For amorphous PDCs obtained at pyrolysis temperatures $\sim > 800^\circ\text{C}$, the conductivity increases with the temperature at which it is measured showing the typical semiconducting behavior.

Metallic-like (electron) conduction with σ_{dc} , as high as 0.1 – 1 ($\Omega \cdot \text{cm}$)⁻¹ is found in $\text{CH}_3\text{SiO}_{1.5}$ -derived Si-C-O pyrolyzed at high temperatures ($T > 1400^\circ\text{C}$) when a percolation network of C_{free} is formed. For high-carbon Si-C-O, such as those obtained from a phenyl-containing polysiloxane, the development of a continuous C network occurs at a lower temperature (1100°C).³⁷² A similar evolution of the electrical conductivity with the pyrolysis temperature is found for the Si-C-N system. For high C-containing Si-C-N ceramics pyrolyzed at temperatures above 1000°C , the graphitic-like carbon is shown to be the main conductive phase.³⁷⁴⁻³⁷⁶ For poly(hydridomethyl)silazane-derived Si-C-N ceramics three temperature regimes can be distinguished.³⁷³ From 1000° to 1400°C the conductivity increases up to three orders of magnitude. This finding is attributed to the loss of residual hydrogen accompanied with an increase in the sp^2/sp^3 ratio of the carbon atoms. Above 1400°C a pronounced increase in conductivity is observed and is attributed to both the formation of nanocrystalline SiC and the reduction of the N-content in the amorphous matrix. Finally, above 1600°C , the material is composed of a mixture of SiC and Si_3N_4 and the nanocrystalline SiC particles were found to be responsible for the increase of σ_{dc} by formation of percolation paths throughout the sample.

The conductivity of PDCs can also be changed by adding filler particles to the preceramic matrix. For example, the addition of MoSi_2 to methyl-containing siloxanes leads to the drastic increase (up to 14 orders of magnitude) in the σ_{dc} of the $\text{MoSi}_2/\text{Si-O-C}$ composites by the formation of percolation paths through MoSi_2 particles.^{271,371} In a more recent paper, MW-CNTs have been homogeneously dispersed into an insulating polysilazane-derived SiCN with a corresponding increase of the electrical conductivity up to 7 orders of magnitude for a volume fraction of CNTs $< 1\%$.³⁷⁷

Information about the nature of the conduction mechanism in amorphous PDCs is obtained from temperature and frequency dependences of the corresponding conductivities, i.e. $\sigma_{dc}(T)$ and $\sigma_{ac}(\nu, T)$. A majority of the experimentally obtained

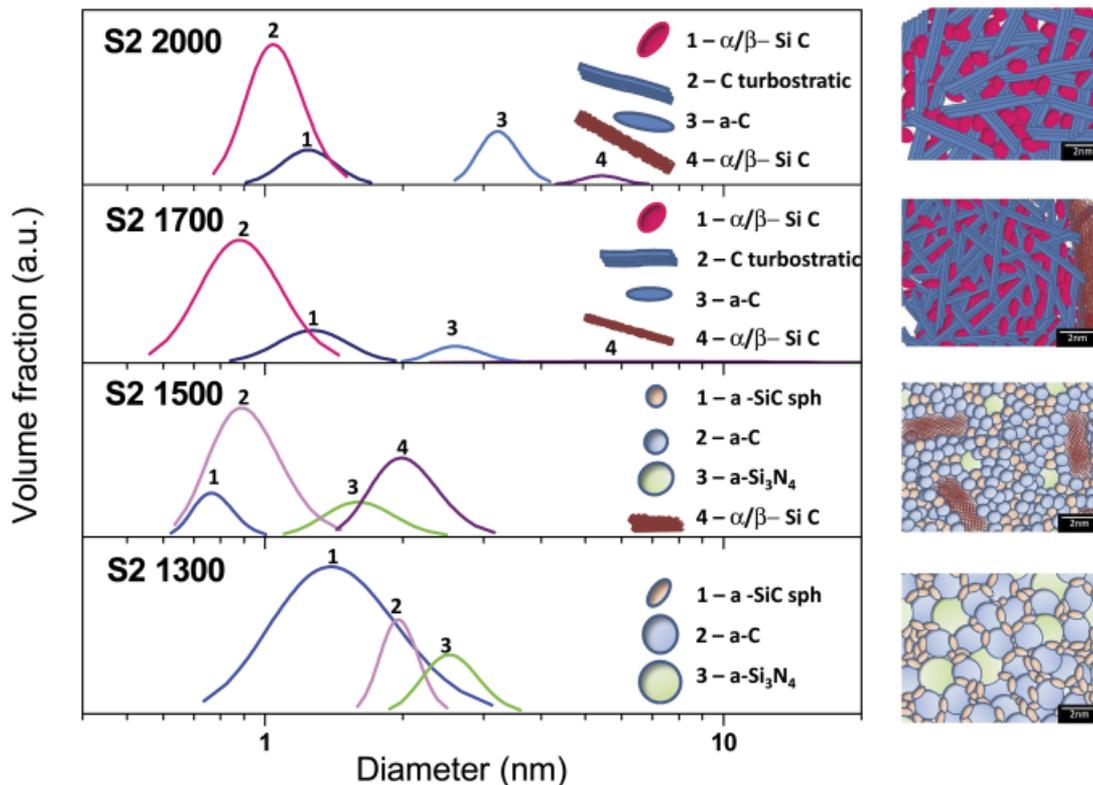


Fig. 16. Results of the simulation of the particle size distributions in the SiCN ceramics annealed at different temperatures as based on the experimental small-angle X-ray and neutron scattering data.³²⁰

$\sigma_{dc}(T)$ and $\sigma_{ac}(v, T)$ dependences for the midtemperature region (amorphous PDCs) indicate that the variation of conductivity with inverse temperature exhibited nonlinear behavior, which indicates that conductivity is due to hopping of carriers between localized states in the mobility gap. It was found that the conductivity of both as-pyrolyzed and annealed samples exhibited a linear behavior when plotted against $T^{1/4}$, which is typical of three-dimensional variable range hopping (3D VRH).^{373,378} This indicates that the conduction occurs by phonon-assisted hopping between localized states. Also the temperature dependence of $\sigma_{ac}(v, T)$ proves that the hopping occurs near the Fermi energy and not near the mobility edges.

Recently, Wang *et al.*³⁷⁹ while investigating the temperature dependence of the conductivity for an amorphous polymer-derived SiCNO ceramic, found that the conduction follows a

band tail hopping mechanism rather than a VRH, as proposed previously.

A rather new finding is the ultrahigh piezoresistivity, i.e. the change of the electrical resistivity due to an applied stress, shown by amorphous PDCs.³⁶⁶ The piezoresistive coefficients of a polymer-derived silicon carbonitride (SiCN) has been reported to be ~ 1000 – 4000 , values which are much higher than those of any existing ceramic. It has been proposed that the piezoresistive behavior follows the tunneling-percolation model with the formation of conductive graphene sheets within the framework of the nanodomain structural model of PDCs as proposed by Saha *et al.*³⁵³

Piezoresistivity has also been found in a SiCO ceramic derived from a commercial methyl-containing polysiloxane pyrolyzed at 1400°C .³⁶⁷ In this study, a high strain sensitivity (k factor)

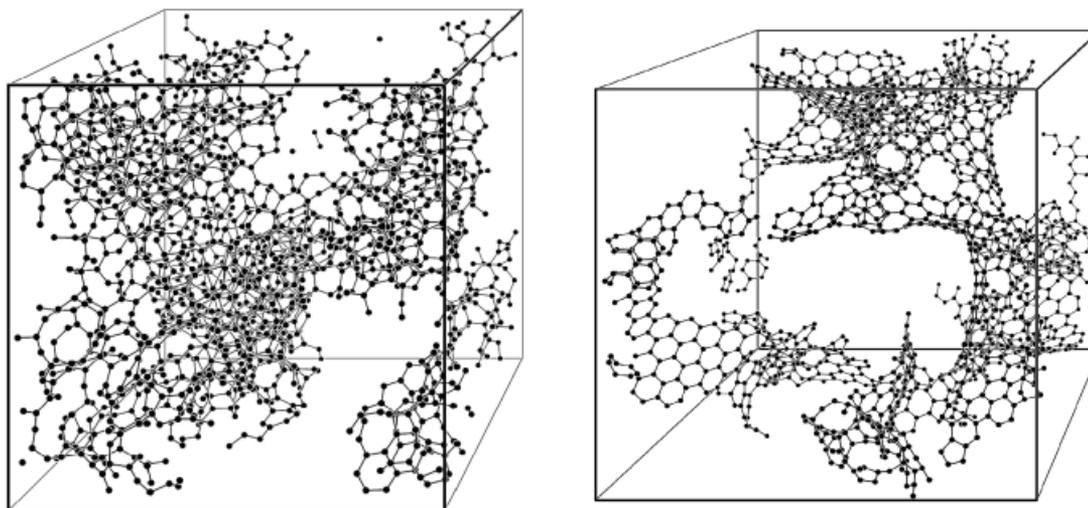


Fig. 17. (a) Separation into amorphous C-rich domains in the SiCN system.³⁵⁵ Only the carbon atoms are displayed. The cubic simulation box at the end of the simulated annealing has side lengths of 33 Å. (b) Monoatomic graphitic layers in the SiCN system.³⁵⁵ Only the carbon atoms are displayed. The cubic simulation box at the end of the simulated annealing has side lengths of 43 Å.

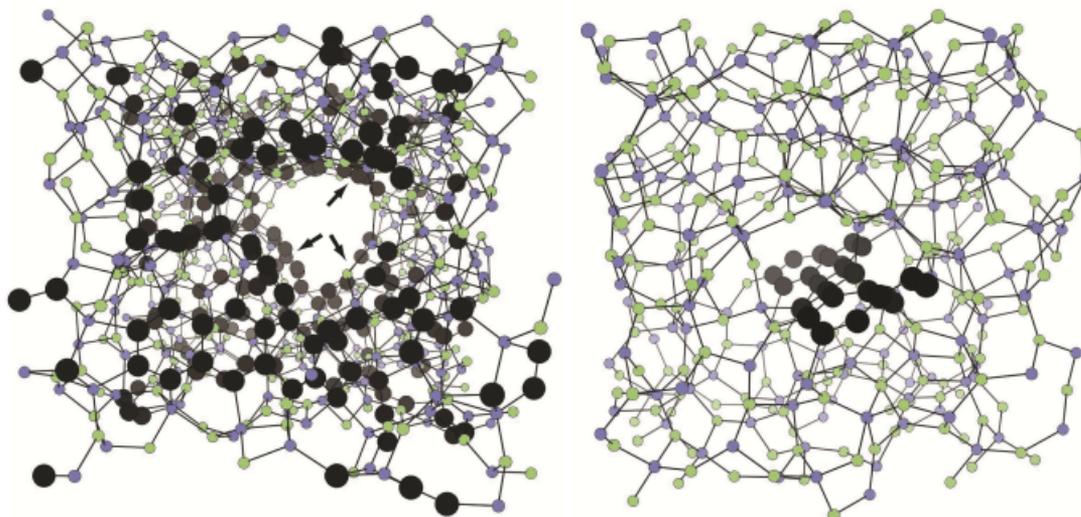


Fig. 18. Models for the segregation of carbon phase in SiCN ceramics.³⁶¹ (Images courtesy of P. Kroll).

of 145 has been measured. The effect has been related to the presence of a percolating network of electrical conductive free carbon in agreement with the proposed tunneling-percolation mechanism. However, contrary to SiCN, for SiCO electrical resistance rises upon applying increased compressive stress. Figure 19 shows the piezoresistivity behavior of SiCN and SiCO PDCs.

The tunable electrical properties, high piezoresistivity, together with the micro fabrication capability and excellent high-temperature thermal and mechanical properties, make the polymer-derived Si-C-N and Si-O-C excellent candidate materials for high-temperature sensors and ceramic MEMS for high-temperature/corrosive-environment applications,²⁹⁰ micro glow plugs^{30,381} and electrode materials for Li-ion batteries.³⁸²⁻³⁸⁴

(2) Magnetic Properties

Iron-containing PDCs with interesting magnetic properties have been reported in the literature following different approaches. In the simpler method composites consisting of particles of α -iron dispersed in SiCN have been fabricated either by incorporating Fe₃O₄ powder into liquid polysilazane precursor Ceraset[®] followed by reduction with graphite³⁸⁵ or starting from Fe powder followed by thermal annealing at 1100°C under argon.³⁸⁶ In the latter case a soft ferromagnetic micrometer-sized iron SiCN composite with a high M_s of ~ 57 emu/g has been obtained. Ceramic foams of silicon oxycarbides (SiCO) possessing magnetic functionalization have been produced from a preceramic polymer and iron silicide filler.²⁷³ The final iron silicide phase consisted of fine cubic Fe₃Si particles embedded in a SiCO matrix and exhibited a M_s in the range of 9.5–17 emu/g, depending on the amount of filler introduced.

A more elegant approach to produce PDCs with magnetic functionalities comprises the incorporation of the metallic iron atoms in the backbone of the polymeric precursor. Ferrocene is probably the most prominent example of an organometallic species.

Manners and colleagues reported the successful ROP of strained silaferrocenophanes, yielding soluble high-molecular-weight polyferrocenylsilanes that can be further pyrolyzed at 1000°C under nitrogen to form a PDC containing ferromagnetic α -Fe crystallites embedded in a C/SiC/Si₃N₄ matrix.^{387,388} Cross-linked poly(ferrocene) obtained from spirocyclic ferrocenophane is a high ceramic yield precursor (up to 90%)³⁸⁹ and its pyrolysis at lower temperatures (600°C) resulted in the formation of smaller, superparamagnetic Fe clusters, while at higher temperatures (900°C) the clusters become larger and thus display ferromagnetic behavior.³⁹⁰

High ceramic yields can be obtained from the pyrolysis of hyperbranched poly(ferrocenylene)s containing Group 14 and 15 elements.³⁹¹⁻³⁹³ Upon pyrolysis, the polymers form mesoporous conductive magnetoceramics with higher iron contents than their linear counterparts. The resulting ceramics are highly dependent on composition and pyrolysis conditions. While pyrolysis of the Si-containing polymers at 1000°C under nitrogen yields ceramics containing mostly α -Fe nanoparticles, those of Ge- and Sb-containing polymers are completely transformed into their iron-alloys. The ceramics from the P-containing polymers show diffraction patterns of iron phosphides. Larger iron silicide nanocrystals are obtained when the pyrolysis is conducted at a high-temperature of 1200°C under argon. This ceramic is highly magnetizable (M_s up to ~ 51 emu/g) and shows near-zero remanence and coercivity.³⁹¹

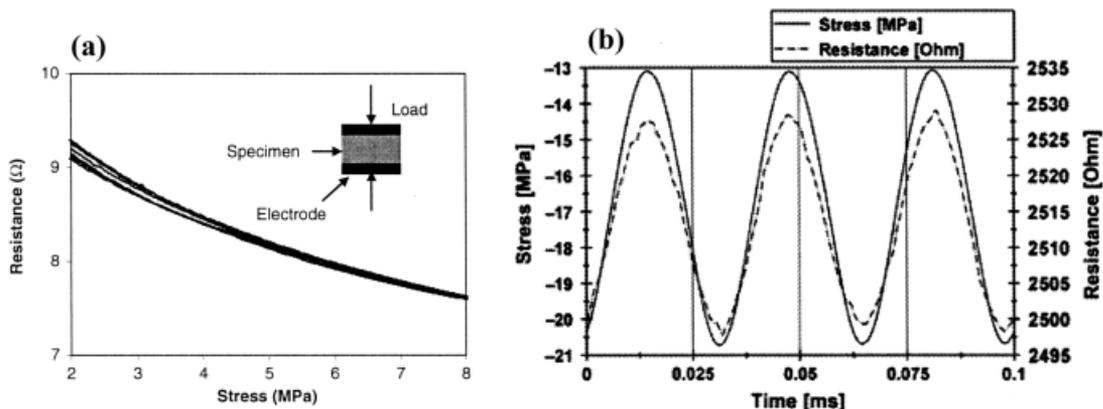


Fig. 19. Experimental proof of piezoresistivity response of (a) SiCN³⁶⁶ and (b) SiCO.³⁶⁷

Co-containing PDCs have been obtained from the complexations of the acetylene moieties of hyperbranched polyynes with cobalt carbonyls $\text{Co}_2(\text{CO})_8$ and $\text{CpCo}(\text{CO})_2$.³⁹⁴ The inorganic–organic hybrid materials are converted into nanostructured cobalt ceramics after pyrolysis at 1000°C under nitrogen with char yields up to $\sim 65\%$. The resulting ceramics are highly magnetizable (M_s up to ~ 118 emu/g) and show near-zero remanence and coercivity (H_c down to ~ 45 Oe). Co-containing SiCOs have also been reported.³⁹⁵

(3) Optical Properties

Optical properties of PDCs have received little attention since PDCs are generally black. Indeed, for the ternary Si–C–O system, this particular feature caught so much the attention of the researchers that silicon oxycarbide glasses have also been called “Black Glasses.”¹¹⁴ The reason for the black color of PDC has been generally ascribed to the presence, in the ceramic structure, of sp^2 C atoms, which form absorbing graphene layers. For these reasons, optical properties of PDCs are scarcely exploited since the absorption of visible light hinders the capability of PDCs for the production of optical devices.

The possibility of carefully controlling the chemical composition of SiCO glasses with the aim of minimizing the presence of “free” carbon to produce a transparent stoichiometric SiCO has been studied by Soraru and colleagues using precursors with Si–H functionalities.^{396–398} The role of Si–H groups in the starting polymer is twofold: it allows reducing the C content and it provides a reactive moiety during pyrolysis for the incorporation of C into the inorganic network with the formation of new Si–C bonds.¹¹⁵ Accordingly, transparent bulk SiCO glasses in the form of small discs, 4–5 mm in diameter and 500 μm thick have been produced from siloxane networks obtained by the sol–gel method using a mixture of triethoxysilane (TEOS) and methyldiethoxysilane.³⁹⁹ The most transparent glasses exhibit an optical absorption edge at 500–550 nm. Photoluminescence (PL) spectra of these glasses show a broad luminescence band centered at about 500 nm, which has been assigned to the presence of sp^2 C clusters. The concentration of these clusters seems high enough to give an intense luminescence but at the same time sufficiently low to allow a good transparency of the resulting glass. The synthesis of the preceramic networks through the sol–gel process facilitates the introduction of extra elements by dissolving them in the starting solution. Accordingly, Zhang et al.⁴⁰⁰ introduced Eu ions in a SiCO glass by adding $\text{Eu}(\text{NO}_3)_3$ to the precursor solution. Eu^{3+} -based luminescence was observed up to 400°C . At higher pyrolysis temperatures a broad blue emission band, centered around 450 nm was formed due to *in situ* reduction of Eu^{3+} – Eu^{2+} . The same approach was used to synthesize a transparent nanostructured erbium activated SiC/SiO₂ nanocomposites by annealing at 1200° – 1300°C a stoichiometric Er-containing SiCO glass. The Er^{3+} was introduced in the sol–gel solution using $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$. The characteristic emission peak of the $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ Er^{3+} transition at 1.55 μm was observed, and its intensity increased both with the pyrolysis temperature and with the Er concentration.⁴⁰¹

Bulk, transparent Si_{nc}/SiO₂ nanocomposites were obtained by high-temperature annealing of TEOS-derived silica-based glasses.⁴⁰² During pyrolysis, the Si–H moieties present in the precursor gel reacted to produce H₂ and Si–Si bonds which above 1000°C reorganize and form Si nanocrystals embedded in the residual silica matrix. The Si_{nc} size was found to be in the range of 3.0–4.4 nm with a corresponding PL in the range 600–800 nm. Most of the sol–gel precursors used for the synthesis of bulk components already described have been used to obtain thin films by the spin coating method. Their optical properties have also been characterized. Si_{nc}/SiO₂ thin films have been obtained on Si substrate by spin coating a TEOS-derived sol–gel solution.⁴⁰³ Karakuscu et al.^{380,404} studied the synthesis of SiCO thin films containing Si, SiC, and C nanoclusters. In general, low pyrolysis temperatures (800° – 1000°C) yield UV-blue luminescence, whereas high-temperatures favor green–yellow luminescence. For Si-rich SiCO films, intense white luminescence was obtained with a broad emission from 430 to 900 nm and an external quantum efficiency of 11.5%. C-rich SiCO films did not show noticeable luminescence due to absorption by carbon clusters (Fig. 20).

Pivin extensively studied the formation and the luminescence behavior of ceramic films obtained by C or Au ion irradiation of preceramic polymers such as polysiloxanes, polycarbosilanes, or sol–gel-derived films.^{305,405} This process does not involve heating the sample and it is a valid alternative to the thermal conversion in case a limitation in the maximum temperature exists. A strong yellow PL emission was observed when the energy transferred by the ions to electron shells of target atoms is within the range of 20–60 eV/atom. This PL was assigned to the segregation of C clusters into an amorphous Si_xO_yC_z matrix. For larger energy transfers the PL shifts toward red and then vanishes, because of the growth and percolation of the quantum dots.⁴⁰⁵ The same thermal conversion process by ion irradiation has been applied to obtain Er^{3+} -doped Si_{nc}/SiO₂ thin films from TEOS-derived gels, which showed good PL properties.⁴⁰⁶

The synthesis and the luminescence behavior of SiCON and SiCN polymer-derived ceramic powders have also been reported.^{313,407} In both cases the maximum luminescence intensity was found for pyrolysis temperatures in the range 500° – 600°C and those measured from dangling bonds³¹³ or from mixed Si–C–N–O tetrahedral units.⁴⁰⁷

(4) Chemical Properties

(A) Oxidation Resistance: PDCs have been initially developed for high-temperature applications and therefore their oxidation resistance has been the subject of many investigations. A review on this subject has been recently reported.⁴⁰⁸

The oxidation of PDCs belonging to the Si–C, Si–C–O, Si–C–N, Si–B–C–N systems has been extensively studied. In general, for PDCs pyrolyzed at a temperature high enough to completely remove the hydrogen from the system, parabolic oxidation rates are observed.^{409–413} These studies showed the formation of a dense and continuous oxide layer (without bubbles or cracks), with a sharp oxide/ceramic interface. The parabolic constants

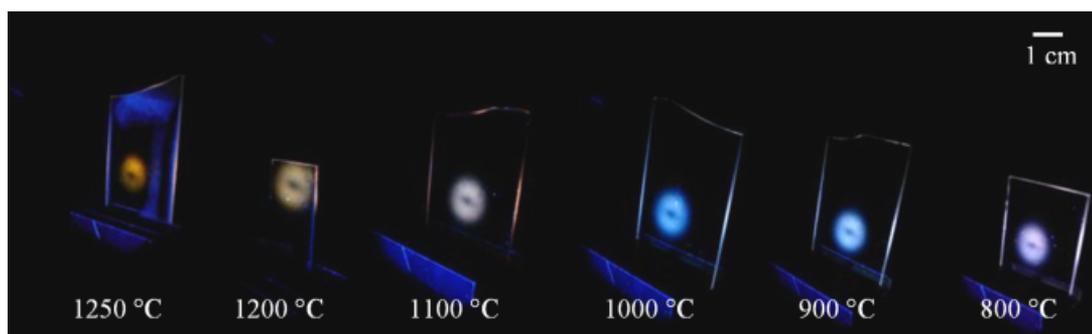


Fig. 20. Photograph of the Si-rich SiCO thin films pyrolyzed from 800° to 1250°C under UV laser excitation. The exposure line differs for each photograph.³⁸⁰

and the activation energies (E_a) were found to correspond to the values obtained for pure SiC and Si₃N₄.^{340,409} Modena and colleagues, while studying the oxidation kinetics of SiCO glasses with different amounts of “free” C (from ~0% up to 60%) found that the parabolic αK_p constants increase with the amount of “free” C present in the nanostructure. This result suggests that the C activity in SiCO glasses is likely less than unity. Recent calorimetric measurements of heats of dissolution in a molten oxide solvent showed that SiCO glasses possess a negative enthalpy relative to their crystalline constituents (silicon carbide, cristobalite, and graphite) in agreement with the proposed lower activity (<1) of C_{free} in SiCO PDCs.⁴¹⁴ Similar results, showing a negative enthalpy of formation, have also been reported for SiCNO derived from polysilazanes.⁴¹⁵ The interpretation which has been proposed to explain the higher stability of Si-based PDCs compared with the crystalline counterparts takes into account the role of the mixed Si_xO_{4-x} units at the interface between the amorphous SiO₂/Si₃N₄ clusters and the graphene layers.^{414,415} In the case of carbon-rich SiCN ceramics derived from polysilylcarbodiimides, where no mixed binds are present (see microstructure chapter), the calorimetric measurements of heat of oxidative dissolution in a molten oxide solvent show that these amorphous SiCN ceramics produced at 1000° or 1100°C possess a small positive or near zero enthalpy of formation relative to their crystalline constituents, namely silicon nitride, silicon carbide, and graphite.³³⁵ These results suggest that the enthalpy of formation for PDCs depend to a great extent on the presence of mixed bonds in the atomic structure.

Studies have also dealt with the influence on the oxidation behavior after the addition of extra elements to SiCN PDCs. The role of boron seems complex. The exceptionally low oxidation rates initially reported for Si–B–C–N ceramics⁴¹⁶ might have been underestimated for several reasons, e.g., the low oxide/ceramic volume ratio, the borosilicate viscous flow and/or the B₂O₃ volatilization). Indeed, more recent studies reported K_p (or αK_p) values close to those for SiC and Si₃N₄ at 1500°C.⁴¹⁷ The addition of Al to Si–C–N–(O) PDCs results into a nonparabolic oxidation curve (at $T \geq 1000^\circ\text{C}$) which decreases more rapidly with time, down to a negligible level.⁴¹⁸ At $T = 1400^\circ\text{C}$, a stationary parabolic rate is observed for $t > 20$ h, with parabolic constants about ten times lower than those of the Al-free Si–C–N samples. The influence of Zr addition on the oxidation of Si–C–N–O PDCs has been studied by Saha *et al.*⁴¹⁹ A parabolic regime was observed for both materials and αK_p for Si–Zr–C–N–O was about half the value for Si–C–N. The lower oxidation rate was related to the lower carbon activity for the Zr-containing system.

(B) Chemical Durability: The chemical durability of silicon oxycarbide glasses with different amounts of “free” C has been studied by Sorarù *et al.*⁴²⁰ in highly basic or acidic (HF) solutions. The SiCO network exhibits greater durability than the pure silica glass, SiO₂, in both basic and acidic media because of the character of the bonding (Si–C bonds are less prone to nucleophilic attack) and a higher degree of compositional disorder and network cross-linking carbon (either bonded to Si atoms or present as a “free”-carbon phase, impedes reactant transport locally). If the SiCO is pyrolyzed at high-temperatures ($T \geq 1200^\circ\text{C}$) it undergoes a phase separation into SiO₂-based, SiC and carbon regions and the chemical durability decreases since the SiO₂ species can be extracted.⁴²⁰ Indeed, if a well-separated SiCO glass is etched for a long time (~6 h) with a highly concentrated HF solution (~20%), the SiO₂ phase can be completely extracted leaving behind a highly porous oxycarbide-derived carbon, with specific surface area values as high as 700 m²/g and high pore volume up to 1.2 cm³/g.^{327,354,421}

(5) Mechanical Properties

(A) Fibers: Historically, the interest in the polymer pyrolysis route to advanced ceramics (PDC route) was driven by the search for ceramic fibers with high thermo-mechanical performance.^{14,27} Yajima *et al.*²⁷ in his famous paper showed

that SiC fibers with tensile strength and Young’s modulus up to 6.2 and 440 GPa, respectively, could be produced. Nicalon fibers produced by Nippon Carbon by the Yajima process are derived from polycarbosilane. The first generation of Nicalon fibers was cured in air at around 200°C thereby introducing up to 12 wt% oxygen into the system. The corresponding fibers were better described as Si(O)C fibers. The oxygen was found to be detrimental for the high-temperature stability and creep. Indeed, oxygen forms a silicon oxycarbide phase which decomposes above 1200°C leading to a weight loss, to the growth of SiC crystals and to strength degradation.^{31,422} These fibers showed a room temperature strength and elastic modulus of up to 3 and 200 GPa, respectively. In order to decrease the oxygen content and to increase the high-temperature stability a new curing process by ion irradiation was developed. Accordingly, the high-temperature stability was increased by about 100° up to 1350°C and the elastic modulus rose to 280 GPa. More recently, through a careful control of the chemical composition, near stoichiometric SiC fibers have been reported with properties much closer to bulk SiC. For these fibers the strength is retained up to 1400°C, the breaking strength reaches 2.5 GPa and the elastic modulus 400 GPa.⁴²³ In the search for increasing the thermal stability of Nicalon-derived SiC fibers, the modification of polycarbosilane with a Ti alkoxides has been proposed by Yajima *et al.*⁴²⁴ and has led to the development of Si–Ti–C–O fibers with high-temperature resistance above 1200°C and room temperature tensile strength and elastic modulus of 3 and 220 GPa, respectively.⁴²⁵ Following the same concept Al- and Zr-modified SiC fibers have been reported, in particular the SiAlCO fibers show tensile strength and elastic modulus of 2.5 and 300 GPa, respectively, and retain their mechanical properties up to 1900°C.⁴²⁶ A complete review on SiC-based PDC fibers has been reported in the literature.²¹²

Fibers of the BN and SiBCN systems have also been synthesized and characterized. SiBCN fibers have been developed from a boron-modified polysilazane; they remain thermally stable up to 1500°C, and have a tensile strength of 1.3 GPa and elastic modulus of 170 GPa.⁴²⁷ Highly dense BN fibers can be obtained from a poly(methylamino)borazine and after pyrolysis at 2000°C they show a tensile strength of 1.5 GPa and elastic modulus of 365 GPa.⁴²⁸ Si–Al–O–N fibers have been obtained by pyrolysis in flowing NH₃ of a polyaluminocarbosilane, PAIC.⁴²⁹ They displayed tensile strength up to 1.75 GPa. The properties of selected Polymer-derived fibers are reported in Table V.

(B) Bulk Samples: Except for fibers, the study of mechanical properties of PDCs has been hindered mainly due to the limitation in the fabrication of suitable bulk test specimens. Two methods have been developed to process small bulk PDC samples: in the first one (powder route) dense, crack-free, monolithic PDCs are produced by direct pyrolysis of green compacts obtained by warm pressing partially cross-linked preceramic polymers^{23,430}; the second one (liquid route) is based on casting either a sol–gel solution⁴³¹ or a liquid polymer²⁵¹ and allows to produce fully dense, small rods or thin plates suitable for flexural strength and fracture mechanics measurements. Two systems have been investigated in some detail: the Si–C–O, derived from sol–gel precursors⁴³¹ or from siloxane resins⁴³² and the Si–C–N derived either from the commercially available liquid poly(ureamethylvinyl)silazane, PUMVS, (Cereset[®] from Kion Corporation)^{251,252} or from other polysilazanes.⁴³³ For both Si–C–O and Si–C–N systems, mechanical properties have been measured at different pyrolysis temperatures while a systematic investigation of the influence of chemical composition has been studied in some details only for the SiCO system.^{431,434} A summary of the measured mechanical properties on the SiCN and SiCO systems is reported in Table VI.

(a) Elasticity and Density: Elastic modulus, E , of SiCNs and SiCOs falls in the broad range of ≈ 80 –155 GPa (SiCNs)^{251,252,433,436,442} and ≈ 57 –113 GPa (SiCOs).^{431,432,440} These values are well below the elastic modulus of crystalline SiC and Si₃N₄ and reflect the rather open structure of the PDC networks. The open amorphous structure of SiCNs and SiCOs also leads

Table V. Tensile Strength, Elastic Modulus and Density of Polymer-Derived Ceramic Fibers

System	Precursor	Tensile strength, σ_F (GPa)	Elastic Modulus, E (GPa)	Density, ρ (g/cm ³)	References
Si(O)C	Polycarbosilane	3	200	2.55	Hasegawa <i>et al.</i> ⁴²²
SiC	Polycarbosilane	2.5	400	3.05	Takeda <i>et al.</i> ⁴²³
Si–Ti–C–O	Polytitanocarbosilane	3	220	2.35	Yajima and colleagues ^{424,425}
Si–Al–C–O	Polyaluminocarbosilane	3	300	3.0	Ishikawa <i>et al.</i> ⁴²⁶
Si–B–C–N	B-modified polysilazane	1.3	170		Bernard <i>et al.</i> ⁴²⁷
BN	Poly[(methylamino)borazine]	1.48	365	1.95	Bernard <i>et al.</i> ⁴²⁸
Si–Al–O–N	Polyaluminocarbosilane	1.75	—	2.6	Soraru <i>et al.</i> ⁴²⁹

to the low density values, in the range of 1.85–2.35 g/cm³ (for both SiCN and SiCOs systems), and has also been substantiated by modeling the structure through molecular simulation.^{363,443}

As a general trend, the elastic modulus and density increase with the pyrolysis temperature due the increased network connectivity realized by stripping the hydrogen present in residual C–H bonds.^{251,431,438} The effect of chemical composition on the elastic modulus and density of sol–gel-derived SiCO glasses has been reported^{431,434} showing that density and Young's modulus increase with the amount of C inserted into the silica network via Si–C bonds.⁴⁴⁴

(b) Poisson's Ratio: The Poisson's ratio, ν , has been reported for a limited number of PDCs and the values are generally quite low. For the SiCN system it ranges from 0.21 to 0.24²⁵¹ while an even lower value, $\nu = 0.11$, has been reported for a SiCO glass.⁴⁴⁰ A Poisson's ratio of 0.11 is the lowest reported value for glasses and polycrystalline ceramics and can be explained by the low atomic packing density and high cross-linking degree of silicon oxycarbide glasses.

(c) Hardness: Vickers hardness (HV), of SiCOs ranges from ≈ 5 to 9 GPa.^{431,432,440} Hardness increases by increasing (i) the pyrolysis temperature and (ii) the amount of C inserted into the silica amorphous network.^{431,434} A similar behavior, i.e. higher HV for higher pyrolysis temperatures, has been reported for materials in the Si–C–N system⁴³⁶ and Si(O)C system.⁴³⁸ However, for the SiCN and Si(O)C materials the hardness is higher compared with SiCOs and ranges between ≈ 8 and 15 GPa.^{251,252,433,436–438} For these ceramics the covalent network has a higher cross-linking degree. Because of the low density and open network of the amorphous SiCN and SiCO structure, the deformation mechanism beneath the indenter shows a major contribution of volume densification which leads to the formation of

circumferential Hertzian cone cracks around the indenter impressions.^{431,439} This behavior is less pronounced for the SiCN system which has a more interconnected covalent network compared with the corresponding SiCO system. Moreover, by increasing the pyrolysis temperature in both SiCO and SiCN systems, the dehydrogenation of the amorphous ceramic leads to a more interconnected network, which in turn, results into a lower contribution of the volume densification and a higher contribution of the shear deformation. The change in the deformation mechanism beneath the indenter is responsible for the observed change of the fracture pattern from the “anomalous” one—with the Hertzian cone crack—at a low temperature to a more “normal” one—with the typical formation of the Radial/Median crack systems—at high temperatures.⁴³⁴ A significant increase in the hardness of the amorphous materials SiCN has been found at increasing indentation load.⁴⁴⁵ This strain hardening behavior has been explained taking into account that the progressive plastic deformation by densification at increasing loads will simultaneously reduce the capability of the deformed material for further densification.

(d) Fracture Toughness: Fracture toughness, K_{IC} , has been measured for a number of SiCN and SiCO PDCs both processed by the liquid and by the powder route. Values between 0.56 and ≈ 3 MPa · m^{1/2} have been reported^{432,433,435,437–439} irrespective of the PDC system. Higher values, in the range of ≈ 2 –3 MPa · m^{1/2} are reported for SiCN and SiCO PDCs obtained from the powder route and have been associated to an *R*-curve behavior resulting from microstructural aspects related to the processing method.⁴³⁵ K_{IC} values measured for PDCs obtained via the liquid route are in general much lower, in the range of 0.56 and 1.3 MPa · m^{1/2}. A value of 0.70 MPa · m^{1/2} has been reported for a stoichiometric SiCO obtained from a sol–gel precursor⁴³⁹ while values from 0.56 up to 1.3 MPa · m^{1/2} have

Table VI. Summary of the Mechanical and Thermal Properties Measured on Bulk Samples of the Si–C–N and Si–C–O Systems

System	Bulk density, ρ (g/cm ³)	Elastic modulus, E (GPa)	Vickers hardness, HV (GPa)	Fracture strength, σ_F (MPa)	Poisson's ratio (ν)	Fracture toughness, K_{IC} (MPa · m ^{1/2})	Thermal expansion, α ($\times 10^{-6}$ °C ⁻¹)
SiCN (Ceraset)	1.85–2.16 ^{217,†} 2.3 ²⁵²	82–140 ^{251,†} 155 ^{252,†}	8.3–11.3 ^{251,†} 15–26 ^{252,†}	< 1100 ^{252,‡}	0.21–0.24 ²⁵¹	0.56–1.3, ^{435,†} 2–3 ^{436,§}	—
SiCN(NCP200) ^{437,¶}	2.32	110–130	11–15	< 118	—	—	—
SiCN (VT50) ^{433,}	1.95	105	6.1	88–146	—	2.1	3.08–3.96**
SiCN (HVNG/HPS) ^{438,††}	2.6 ^{‡‡}	109–118 ^{††}	7.9–12.8 ^{††}	80–235 ^{††}	—	—	—
Si(O)C (AHPCS) ^{439,§§}	2.3–2.9 ^{§§}	—	9–13 ^{¶¶}	—	—	1.4–1.67	—
SiCO (sol–gel) ^{431,}	1.7–2.28	57–113	4.7–9.3	70–900	—	0.57–0.77 ⁴⁴⁰	3.21 ⁴⁴⁰
SiOC (MK) ^{441,***}	2.23	101	6.4	—	0.11	—	—
SiOC (SR350) ⁴³²	2.35	97.9	8.5	133–612	—	1.8	3.14

[†]Pyrolyzed between 800° and 1400°C. Higher values generally measured at higher pyrolysis temperatures. [‡]Pyrolyzed at 1000°C, 9 h. [§]Properties measured on samples prepared from the powder route. [¶]NCP200 from Nichimen Corp., Tokyo, Japan. Pyrolyzed at 1100°C, 4 h. Berkovich indenter. Samples prepared from the powder route. ^{||}VT50, Hoechst AG, Germany. Pyrolyzed at 1050°C. Samples prepared from the powder route. ^{**}VT50, Hoechst AG. Pyrolyzed at 1200°C. ^{††}HVNG and HPS are two methyl-vinyl-polysilazanes.³⁷¹ Pyrolysis between 1100° and 1550°C for 6 h. Higher values generally measured at higher pyrolysis temperatures. Samples prepared from the powder route. ^{‡‡}Measured at 1400°C, 6 h. ^{§§}AHPCS is an allylhydridopolycarbosilane (Starfire Systems Inc., Malta, NY). Properties measured on samples prepared from the powder route and pyrolyzed at temperature between 1000° and 1600°C, 4 h. ^{¶¶}Higher value (13 GPa) measured at 1200°C and lower value (9 GPa) measured at 1600°C. ^{|||}Higher values are generally measured for the samples with the higher content of carbidic carbon (Si–C) and pyrolyzed at the higher temperatures. ^{***}MK is a polymethylsiloxane from Wacker Chemie GmbH, Germany. Properties measured on samples prepared from the powder route and pyrolyzed at 1100°C, 2 h.

Table VII. Shear Viscosity of Selected PDC Systems. All the η values have been measured at 1553, but the data reported in Zimmermann *et al.*⁴⁴⁸ which have been collected at 1673K

System (precursor)	Shear viscosity, η (Pa · s)	Notes	References
SiC _{0.33} O _{1.33} (sol-gel)	10 ¹³	3-point bending	Rouxel <i>et al.</i> ⁴⁴¹
SiC _{0.47} O _{1.47} (sol-gel)	5 × 10 ¹⁴	3-point bending	Rouxel <i>et al.</i> ⁴⁴¹
Si-C-O (SR350)	3 × 10 ¹³	Compressive creep	Renlund <i>et al.</i> ⁴³²
SiC _{0.67} O _{0.67} (TVTMS/PHMS HP 2073 K)	≈ 10 ¹⁷	Internal friction	Ota and Pezzotti ⁴⁴⁶
SiAl _{0.107} C _{0.47} O _{1.86} (MK/Alumatrane)	2 × 10 ¹¹	Compressive creep	Riedel <i>et al.</i> ²²
SiCN (NCP-200)	2 × 10 ¹³	Compressive creep	An <i>et al.</i> ⁴⁴⁷
SiBCN (Polyborosilazane)	≈ 2 × 10 ¹⁵	Compressive creep	Riedel <i>et al.</i> ⁴⁵⁰
SiBCN (Polyborovinylsilazane)	≈ 10 ³ ≈ 10 ¹⁶	Compressive creep	Zimmermann <i>et al.</i> ⁴⁴⁸

All the η values have been measured at 1553 K, but the data reported in Zimmermann *et al.*⁴⁴⁸ which have been collected at 1673 K.

been measured on a liquid-derived fully dense SiCN pyrolyzed at temperatures from 800° to 1300°C, respectively.⁴³⁷

(e) Viscosity, Viscoelasticity, and Creep: Si-based PDCs exhibit a remarkable creep resistance. Creep is very limited up to 1300° and 1550°C for Si-O-C and Si-(B)-C-N PDC, respectively. Viscosity of amorphous PDC is possibly the property that makes these materials remarkably different from any other ceramic known so far being, typically, two to three orders of magnitudes higher than vitreous silica and certainly the highest measured value for a glass at high temperatures. Data on Si-O-C glasses were obtained from bending creep⁴⁴¹ and internal friction experiments⁴⁴⁶; on amorphous Si-C-N,⁴⁴⁷⁻⁴⁴⁹ Si-Al-O-C,²² and Si-B-C-N^{448,449} were also reported from compressive creep experiments.

The viscosity, η , of Si-C-N⁴⁴⁷ is close to that of Si-O-C⁴⁴¹ while Si-B-C-N is slightly more refractory.⁴⁵⁰ A glass transition temperature, T_g , of 1350°C, identical to that reported earlier,⁴³² has been measured for a sol-gel-derived silicon oxycarbide glass with composition: SiO_{1.39}C_{0.32} by extrapolating the viscosity to the conventional viscosity range of 10¹²–10^{12.6} Pa · s associated with the glass transition.⁴⁴¹ The addition of aluminium to produce SiAlOC glasses results in a decrease of η .²²

The shear viscosity of PDCs is reported in Table VII.

A visco(an)elastic behavior for SiCO glasses has been suggested from internal friction measurements⁴⁴⁶ and then reported based on compressive stress tests performed at temperatures in the range 1000°–1200°C.⁴⁵¹ It has been proposed that the relaxation occurs via viscous flow in oxygen-rich regions with an atomic organization resembling that of amorphous silica through channels existing between a graphene network. Accordingly, the inelastic behavior in these complex nanostructured amorphous materials would find its source in the load transfer from the silica (which experiences viscous flow in this temperature range) and the graphene network. When the stress is relieved, the elastic energy stored in the graphene regions is the driving force for the strain recovery.

VI. Applications of PDCs

Because of their physical-chemical and functional properties as well as their ability of being shaped using a wide variety of processing methods, PDCs have found application in several key fields such as information technology, transport, defense, energy as well as environmental systems, biomedical components and micro- or nanoelectromechanical systems (MEMS/NEMS). Only selected applications will be discussed here.

(1) Fibers

Ceramic fibers constitute the oldest and most successful commercial application of preceramic polymers. Several developments occurred in the field, which led to enhanced properties and the formation of preceramic polymer-derived fibers en-

abling components for ceramic matrix composites. Advancements in processing methods allowed a decrease in oxygen contamination from ~15 to <0.5 wt%, with significant improvements in terms of high-temperature stability while at the same time maintaining very good mechanical properties (tensile strength of the order of 2.6–3.3 GPa), with prices in the range of 1000–7000 euros/kg.⁴⁵² Furthermore, the incorporation of B and N allowed for the synthesis of fibers that remain amorphous at temperatures up to ~1700°C in inert atmospheres, with strengths equaling those of SiC-based fibers, with superior oxidation and creep resistance.⁴⁵³ Other recent developments include the fabrication of BN fibers⁴⁵⁴ and of SiCN fibers containing multiwalled CNTs; in the latter, the addition of 1 wt% MWCNTs led to an increment of 100% in tensile strength for green fibers⁴⁵⁵ and 50% for pyrolyzed ones.

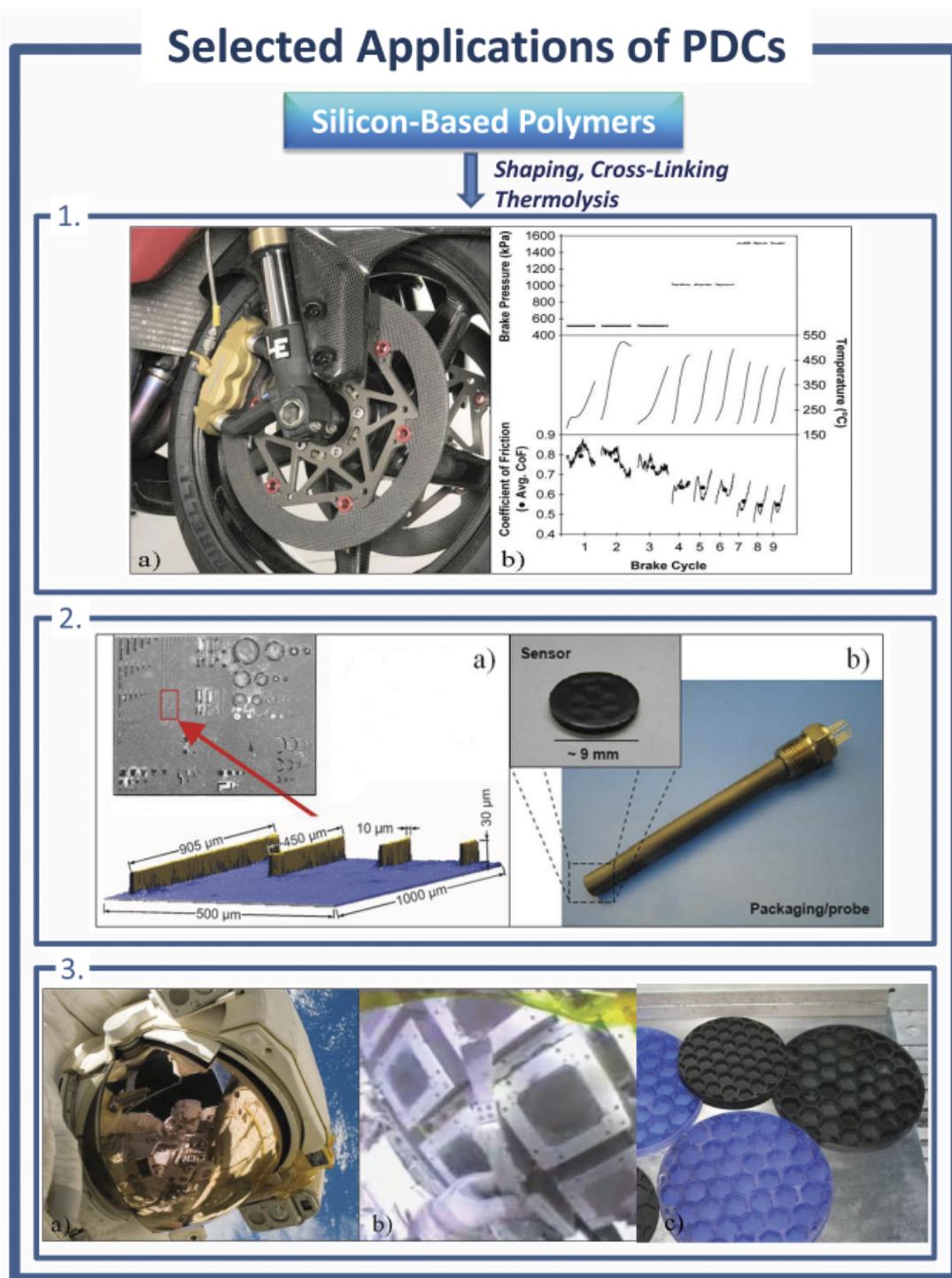
Polycarbosilane doped with titanium alkoxide has been used to fabricate thin fibers and mats. Upon heat treatment in air, a surface layer consisting mainly of anatase nanosized crystals forms, due to bleeding of the additive.⁴⁵⁶ These components possess an excellent photocatalytic activity, decomposing organic chemicals and coliform bacteria when irradiated with UV light, and have been used for purification of bath water and many types of industrial wastewater.

(2) Ceramic-Matrix Composites

Preceramic polymers (often containing ceramic powder fillers) have been widely used for the manufacturing of ceramic matrix composites. Advantages over competing technologies such as CVI or melt infiltration include simpler, less costly equipment, lower process temperatures (which limits processing damage to the ceramic fibers), shorter cycle times and the capability to produce very large (with thickness >5 cm) and complex parts. An increase in the ceramic yield of preceramic polymers has led to a lower number of infiltration cycles required to obtain parts with acceptable residual porosity, allowing a minimum production temperature of ~850°C. The development of low-to-medium viscosity liquid siloxane-based resins has lowered the overall cost of the composites. Moreover, components can be machined to near-net shape before full densification and no extensive final machining is needed (for example to eliminate fixtures or excess external silicon).⁴⁵⁷ An interesting novel application of these materials is as brake components for high performance motorbikes (see Panel C), with potential for use also in automobiles, trucks, trains, and airplanes. These ceramic rotors, made using a polycarbosilane preceramic polymer with SiC as filler and carbon fibers as reinforcement, are 60%–70% lighter, have a better coefficient of friction (>0.5) and show less wear in comparison with metal ones. They also offer excellent cold friction, are unaffected by moisture, and are resistant to high-temperature performance fade. Their performance is also more consistent than that of more expensive carbon/carbon rotors, and contributes to decreasing weight, improving stopping power and vehicle efficiency, while producing better overall performance.⁴⁵⁸

Panel C. Selected Applications of PDCs

- (a) STARBlade[®] CMC brake rotors fitted on a motorcycle; (b) performance data for the rotor (image courtesy of E. Bongio, Starfire Systems Inc.).
- (a) Inset: different micro-sized test structures produced by direct X-ray lithography of a polycarbosilazane (ABSE)⁴⁵⁵ layer deposited on a ceramic substrate (after pyrolysis at 1200°C). The topography of several bar structures was measured using a confocal chromatic white light sensor. The high aspect ratio and edge precision achievable, for such a precursor, with the direct lithographic technique are outstanding compared with soft lithography and UV lithography (image courtesy of M. Schulz, Research Center Karlsruhe, Germany); (b) image of a commercially available harsh environment sensor and probe (image courtesy of M. W. Usrey, Sporian Microsystems Inc.).
- (a) the reflection in the astronaut's faceplate shows six coupons of heat shield material purposely gouged to simulate possible damage to the heat shield (image courtesy of E. Bongio, Starfire Systems Inc.); (b) application of the NOAX sealant by spatula (image credit: NASA TV, July 12, 2006); (c) Mock-up of space mirror supports (blue: not pyrolyzed; black: pyrolyzed). Image courtesy of A. Hill, United Materials and Systems Inc., <http://www.ceramicore.com>



(3) Highly Porous Components

Preceramic polymers are particularly suited to the production of ceramics possessing a high volume of porosity (<70 vol%), as they can be processed in a large variety of ways to obtain parts with pore sizes ranging from nanometers to several millimeters.²¹⁴ Components with hierarchical porosity (in the micro-, meso-, and macro-pore range) can be achieved by one-pot synthesis, as well as membranes possessing high permeability and selectivity.⁴⁵⁹ Characteristics such as the specific surface area or the electrical conductivity can be varied by adding suitable fillers or modifying the processing parameters. Etching of PDCs (using either hydrofluoric acid for SiCO or chlorine gas for SiC or SiCN) results in carbon-based materials with high specific surface area and a large volume of micro- and meso-pores.^{327,354,460} Applications that have been envisaged and tested for polymer-derived porous ceramics include impact absorption, thermal protection, adsorption, gas separation, and 3D reinforcement for metal-matrix composites.⁴⁶¹

(4) Coatings

One of the most promising areas for the application of preceramic polymers is low-dimensional products such as coatings. Preceramic polymers can be deposited on substrates of various kinds using different deposition techniques based either on a liquid (melt or solution) or a vapor phase. The preceramic polymers can be loaded with different fillers to modify selected properties, as well as to increase the thickness achievable without cracks with one deposition, and the processing temperature can be kept rather low (<800°C) to minimize damage to the substrate. In particular, there is a strong interest in finding low temperature, cost effective ways of protecting metal surfaces against oxidation, wear, and corrosion. Reactions occurring at the interface during processing can also improve adhesion with the metal,⁴⁶² although the formation of brittle phases should be avoided. Coatings containing Si or C clusters have also been developed, potentially for opto-electronic applications.⁴⁶³ Oxidation protection layers have been deposited on C/C composites as well as carbon fibers.⁴⁶⁴ Layers with controlled porosity can be produced by the addition of fillers,⁴⁶⁵ for applications such as catalyst support or biomedical devices. Of particular interest is the use of preceramic layers processed at low temperature (i.e., ambient to <100°C) to coat large surfaces (e.g., train carriages) and form clear, transparent, protective, permanent coatings that do not allow inks, permanent markers, spray paints, stickers and dirt, tree sap and other stains to stick to the surface, while protecting the surface from weathering, corrosion, and oxidation.⁴⁶⁶

Preceramic polymer-based layers have also been successfully applied as joining medium for ceramic monoliths and ceramic matrix composites. In this case, also, the use of fillers is instrumental in achieving good properties and a suitable microstructure of the ceramic interlayer.^{186,215,216}

(5) Microcomponents

The manufacturing of miniaturized ceramic components using the powder route, i.e. pressing or micro powder injection molding, is limited by the cost of the mold while the shaping of bulk ceramics (either sintered or in the green state) does not typically allow to obtain features smaller than 0.1 mm. With preceramic polymers, processed by various lithographic methods, it is possible to realize features below 1 μm in size⁴⁶⁷; however special care during fabrication has to be taken to reduce the shrinkage occurring during pyrolysis, which can cause deformation of the fabricated structures.⁴⁶⁸ Moreover, the excellent thermo-mechanical, oxidation, and corrosion resistance properties of PDCs allow the application of MEMS/NEMS in harsh environments at high temperatures under oxidizing conditions. PDC nano-, and microsystems have found applications in photonics and fluidic devices, and as components for electrical heating (micro igniters or glow plugs), microparts and actuators.^{232,234-236,469} Panel C shows two images, illustrating the high level of complex-

ity achievable in these systems and a commercially available PDC-based sensor that has been developed for monitoring the environment in jet engine turbines and energy generation turbines.⁴⁷⁰

(6) Other Applications

SiCN has emerged as a promising component for anode material in lithium batteries because its chemical stability in corrosive environments could protect graphite from exfoliation during charging and discharging. Moreover, experimental results indicate that the SiCN phase is active in terms of lithium intercalation/deintercalation because it contains disordered carbon that can act as a percolation path for lithium as well as for electrons. SiCN can therefore combine the role of a binder phase for graphite and conductive additive in one material.³⁸³ Furthermore, the introduction of Li into the solid SiCN network can be achieved by lithiation reaction of silazanes, resulting in novel ceramics potentially suitable as Li ion conductors in the batteries.⁴⁷¹ Experiments performed on SiCO did not give similarly encouraging results.³²⁷

The possibility of applying a preceramic polymer-based mixture in the polymeric state, for subsequent *in situ* conversion to ceramic during service, has been exploited in the development, by Alliant Techsystems, NASA JSC, GRC, MSFC, LRC, and Materials Research and Design, of NOAX (Non-Oxide Adhesive, eXperimental). This is a paste-like sealant for repair of small cracks and gouges that can result from damage to the reinforced carbon-carbon composite of the Space Shuttle's wing leading edge or nose cap. It is based on a polycarbosilane preceramic polymer (SMP-10, Starfire Systems, Malta, NY) and contains SiC powder and other fillers. The repair is a simple process that can be performed during an on-orbit extra vehicular activity (EVA) space walk by an astronaut. It has the ability of being applied in a wide range of temperatures (4°–40°C) using a specially designed putty knife and caulk gun in the vacuum of space. It can adhere properly to the substrate on which it is applied, and harden in place; upon re-entry into the Earth's atmosphere it ceramizes when the surface temperature reaches 1650°C and more, without shrinking, cracking or melting. The sealant system was successfully demonstrated for repair of simulated damage during a spacewalk (EVA3 of STS-121 mission). Tiles with simulated damage were repaired on orbit (see Panel C), and two of the test tiles were later subjected to arc-jet tests under re-entry conditions in a NASA facility, and did not show the formation of any cracks in the sealing material. NOAX will therefore likely fly on every flight until the end of the Space Shuttle program.

Silicone resins have also been tested as binders for brake pads, as a substitute for a standard phenolic resin.^{472,473} Recently introduced ceramic composite disks, operating at a much higher temperature than conventional gray cast iron discs and showing higher friction coefficients, require in fact the development of a dedicated class of pads able to sustain the high amount of energy involved in the friction process and the high temperatures reached by the components. The silicone resins tested showed good wettability with the various components constituting the pad (lubricants, abrasives, and heat absorbers) enabling them to be fabricated by warm pressing. In general, polysiloxane resin-based pads showed superior friction behavior as compared with a conventional organic pad, especially at high temperature and at high energy. Increasing the pyrolysis temperature (from 500° to 900°C), the friction coefficient decreased and the wear rate increased, but in general the friction curves decreased their dispersion. Preceramic polymer-based friction modifier resins are also in development at Starfire Systems. They reduce pad wear, improve cold friction, reduce fade and improve braking consistency. Furthermore, they are applied to the surface of conventional brake pads; under intense braking conditions, the material converts from a binder to a ceramic, forming a composite-like matrix together with the other materials present in the pad.

Silicon oxycarbide in combination with a great variety of fillers has also been developed as matrix material for the application as heating elements which withstand high temperatures up to 1300°C, e. g. in novel glow plugs in diesel engines.⁴⁷⁴ Presently, the work is extended to produce shaped ceramics with temperature and pressure sensor (piezoresistive effect).³⁶⁷ Finally, a very recent development enabling the fabrication of defect-free bulk components using a liquid silazane precursor infiltrated in a sacrificial (polymeric) scaffold has led to the manufacture of ceramic space mirror mock-ups which are machinable using conventional computer numerical controlled machine tools and methods (see Panel C).²⁶⁵

VII. Conclusions and Outlook

PDCs are a unique class of materials and are synthesized via the polymer-to-ceramic transformation process of preceramic polymers. In this review we have highlighted silicon oxycarbide (SiCO) and silicon carbonitride (SiCN) based ceramics which can be obtained by the thermal decomposition of poly(organosiloxanes) and poly(organosilazanes) or poly(organosilylcarbodiimides), respectively. The most outstanding feature of polymer-derived SiCO and SiCN materials is the fact that carbon can be dissolved in significant amounts in silica and silicon nitride, which is not possible by conventional solid state reactions or other synthetic approaches.

The presence of carbon in silica and silicon nitride has a great variety of structural and property related consequences: First, carbon hinders the crystallization of SiO₂ and Si₃N₄ up to 1500°C. Boron-containing SiCN exhibits even higher thermal stability and crystallizes at around $T > 1700^\circ\text{C}$ in certain compositions. The amorphous systems show T_g points unusually high compared with pure silica, namely 1350°C for SiCN, $>1800^\circ\text{C}$ for SiBCN, and 1300°C for SiCO.²² This behavior enables to produce materials with an amorphous matrix for high-temperature applications having no grain-boundary controlled and limited materials properties such as corrosion, grain growth, and creep.

Second, the microstructure of polymer-derived SiCO and SiCN ceramics very much depends (i) on the type of preceramic polymer used as a starting compound, (ii) the carbon content of the ceramic obtained therefrom, and (iii) the final temperature and atmosphere of the pyrolysis process and subsequent annealing procedures. It could be shown that at lower synthesis temperatures (1100°C, 0.1 MPa Ar atmosphere), polysilazanes are converted to form single-phase amorphous SiCN while polysilylcarbodiimides result in multiphase amorphous nanostructured composites with so-called nanodomains with 1–3 nm in size mainly comprising amorphous carbon, carbon nitride (CN_x) and silicon nitride. The different amorphous phases could not be resolved or distinguished in TEM so far but are clearly evidenced by solid-state NMR analysis, Raman spectroscopy, and SAXS analysis.

Another important aspect of SiCN ceramics is their tolerance to oxygen. In polycrystalline ceramics, the presence of oxygen severely degrades their high-temperature behavior by forming an intergranular glassy phase, which accelerates mass transport. The difference in the high-temperature behavior between Nicalon and High Nicalon SiC-fibers illustrates the importance of eliminating oxygen to improve the creep resistance and crystallization resistance at high temperatures. In contrast, the nanostructure of amorphous SiCN is intrinsically stable. SiCN ceramics may contain up to several wt% oxygen without any loss of their high-temperature resistance to crystallization and creep.

The distinct nanodomain features of the PDC microstructures have been claimed to cause the unusual high-temperature resistance of amorphous SiCO- and SiCN-based ceramics with respect to creep and crystallization. In addition, calorimetric measurements revealed that amorphous SiCO and some compositions of SiCN have negative enthalpies of formation with

respect to silicon carbide, silicon nitride cristobalite, and graphite. Thus, it can be concluded, that their persistence at high-temperature derives from thermodynamic as well as from kinetic factors.^{335,414,415,475}

The extraordinary thermal stability of SiCO and SiCN PDCs has been the basic motivation in the past to study these materials in more detail, predominantly for high-temperature applications in harsh environments. In recent years, Si-based PDCs have been shown to possess a variety of valuable functional properties in addition to their ultra-high temperature stability. The discovery of the semiconducting^{371–376} as well as the piezoresistive behavior of SiCO and SiCN is related to carbon and SiC segregation during annealing at $T > 1000^\circ\text{C}$ in carbon-rich materials¹⁸² while PL is found in silicon rich PDCs.³⁸⁰ Composites containing mixtures of graphite and SiCO or SiCN show interesting electrochemical properties suitable for applications as anode material in Li-ion intercalation batteries.³⁸⁵ In this case the capacity as well as the rate capability of the novel C_{graphite}/SiC(O)N composites are significantly enhanced compared with those of pure graphite. The perspective of this result is the development of anode materials suitable for high power and mobile energy applications such as electric and hybrid electric vehicles as well as batteries for solar cells (energy storage during the night). Furthermore, the analyzed composite anode revealed an enhanced performance stability and reduced amount of exfoliation of graphite during inter- and deintercalation of solvated lithium ions.

Initially the research on PDCs was focused mainly on dense bulk materials and fibers for mechanical applications at high temperatures. Nowadays, nano powders and porous PDCs with pore sizes in the range between several microns and few nanometers for applications such as catalyst support and for liquid and (hot) gas separation processes are gaining increasingly importance. Moreover, the polymer-to-ceramic transformation is a suitable technology to produce a broad spectrum of ceramic-based composite materials with adjusted chemical, mechanical, and physical properties. PDCs can also be processed to thin films for optoelectronic applications and to thick films, e.g. for hard coatings, environmental barrier coatings, and others. The great flexibility in terms of processing and forming of preceramic polymers into shaped-ceramic components has also enabled them to play an important role in several other applications.

To further investigate and explore the unusual microstructure and physical properties of PDCs in more detail it will be the challenge of future studies in this field, and it requires a strong interdisciplinary approach in basic research and development in chemistry, physics, and materials science and engineering.

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