

A new type of precursor for fibers in the system Si–C

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Abstract

Ceramic fibers with compositions in the system Si–C have a great potential for high-temperature applications. In recent years, our efforts have been dedicated to the development of polymers consisting of polysilanes suitable to spin fibers and build up matrices for CMC as well. The polysilanes are synthesized via disproportionation of the so-called disilane fraction [Richter, R., Roewer, G., Böhme, U., Busch, K., Babonneau, F., Martin, H.-P. *et al.*, *Appl. Organomet. Chem.*, 1997, **11**, 71 (and references cited therein)]. A further thermal treatment yields materials which are soluble in organic solvents, and these solutions can be dry-spun to give fibers which are subsequently pyrolyzed. Solubility and high ceramic yield make this precursor a promising candidate for matrix infiltrations, too. The chemistry and the adjustment of viscosity and solubility to the requirements of the fiber processing as well as the conversion of the dried fibers to pure SiC fibers by thermal treatment will be reported.

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1. Introduction

SiC fibers have been of great interest for high temperature applications for the last 20 years. Yajima *et al.*^{1–4} already obtained polymer-derived SiC fibers in 1975, when they heated dodecamethyl cyclohexasilane (already reported by Burkhard in 1949⁵) in an autoclave, extracted low molecular proportions with acetone, dissolved the high molecular portion with xylene, dry-spun the solution and pyrolyzed the green fibers. A more simple approach, during which the use of an autoclave could be avoided, was invented by the same group of researchers, leading to a polycarbosilane which was meltable and could thus be spun via the melt-spinning process.^{4,6–8} Since the green fibers obtained in this process were still meltable, they had to be cured by heating in air up to 200 °C. This leads to a considerable oxygen content in the SiC ceramic fibers.

Verbeek and Winter applied the synthesis of polycarbosilanes via a radical polymerization of monosilanes for a patent,⁹ a reaction which was first described by Fritz *et al.*^{10–12} The patent of Verbeek and Winter also describes the

manufacture of SiC ceramic fibers via melt-spinning; the curing of the green fibers by heating them in air is usually required.

Many other methods for the preparation of preceramic polycarbosilanes have been reported, for example the Wurtz-like coupling of phenylmethylchlorosilane/dimethylchlorosilane mixtures^{13–15} and of R₂SiCl₂/RSiCl₃ mixtures,¹⁶ the hydrosilylation of vinylsilanes^{17–19} and the ring-opening polymerization of 1,3-disilacyclobutane derivatives with Pt catalysts.^{20–22} They have been summarized in several review articles.^{23–25}

Unfortunately, the fibers commercially available so far (Nicalon, Hi-Nicalon, Tyranno, etc.) either show insufficient stabilities against oxidation or thermal creep due to their rather high oxygen content, or are only available at very high costs due to expensive processing steps such as electron beam curing (e.g. Hi-Nicalon), which prevents their use at a large scale.

Disilane mixtures forming as a high-boiling fraction during the Müller-Rochow process²⁶ as well as their base-catalyzed disproportionation into monosilanes and polysilanes are well-known.^{27–30} Extensive studies of the use of these polysilanes as preceramic polymers were reported by Baney^{31–33} as well as Roewer and co-workers³⁴ (see also

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Refs. 23–25). The manufacture of SiC ceramic fibers from these polysilanes has also already been described.^{35–37} Since the polysilanes are meltable solids, green fibers obtained by the melt-spinning process must undergo a further curing step, so that they retain their shape and do not stick together during pyrolysis. Although this was successful in some cases,^{35,36} the development of a technically running process has met considerable difficulties in the past.

To overcome these difficulties, we have recently developed a process starting with the readily available disilane fraction and yielding oxygen-free SiC fibers, during which a curing step is completely superfluous. The key of this procedure is a further thermal treatment of the initially formed polysilane, which results in a polymer no longer fusible, but still soluble in organic solvents like benzene or toluene. Fibers can be dry-spun from these solutions, and due to the infusibility of the material no further curing step is required before pyrolysis.

From NMR investigations³⁸ it is known that polysilanes undergo further crosslinking as well as partial Kumada rearrangement to polysilane–polycarbosilane copolymers upon heating at temperatures between 350 and 450 °C. Yet, no investigations about the macroscopic properties of these products, aiming at their processability, have been reported.

2. Experimental

Because of the moisture sensitivity of the compounds used in this work, all steps are carried out under inert gas atmosphere (preparation of polymers and polymer solutions under argon, fiber spinning and pyrolysis under nitrogen).

2.1. Preparation of the polymer solutions

The disilane fraction used in this work was purchased from Wacker, Burghausen/Germany, and purified by distillation. The portion boiling at 150–154 °C was used. ²⁹Si NMR spectra showed that it consisted of a 1:1 mixture of 1,1,2,2-tetrachlorodimethyldisilane ($\delta(^{29}\text{Si}) = 18.0$ ppm) and 1,1,2-trichlorotrimethyldisilane ($\delta(^{29}\text{Si}) = 15.6$ ppm, 25.0 ppm). The disproportionation was performed by adding 1–2 wt.% of *N*-methylimidazole as a catalyst and, optionally, 10 wt.% of phenyltrichlorosilane and by heating to 220 °C with a rate of 0.5 K/min. During heating, a distillate consisting of (CH₃)SiCl₃, (CH₃)₂SiCl₂, traces of (CH₃)₃SiCl and higher oligosilanes is obtained. After cooling at room temperature, the dark brown residue is heated to 400 °C with a rate of 3 K/min and kept at this temperature for 50 min. During this procedure, a small amount of a yellow distillate (consisting of monosilanes and oligosilanes) is obtained. The product is then cooled at room temperature, and traces of low molecular weight components are removed under vacuum. The dark brown material is then dissolved in an excess of toluene under reflux, and then a solution of 1 wt.% of polystyrene in toluene is added so that the weight ratio of copolymer:polystyrene is

about 35:1. The viscosity of the homogeneous solution obtained is adjusted to about 2 Pa s by partially removing the solvent under vacuum.

2.2. Fiber spinning and pyrolysis

The polymer solution described above is transferred into a spinning apparatus consisting of a heater block, out of which the material is extruded by a piston through 1–5 spinning nozzles ($\varnothing 150$ μm; $l = 0.45$ mm). The polymer fibers were dried during spinning in a stream of nitrogen at 40 °C and stretched by winding them up on a rotating spool at velocities between 50 and 300 m/min. Fiber bundles with lengths corresponding to the circumference of the spool were obtained by cutting the wound-up fibers. These fiber bundles were then pyrolyzed by pulling them through a vertical tube furnace under nitrogen atmosphere. The furnace contained three heating zones, allowing pyrolysis at a rate of 12 K/min up to an end temperature of 1200 °C.

2.3. Fiber characterization

The oxygen content of the fibers was determined using a hot gas extraction analyser (LECO EF-400); fibers prepared under proper conditions contained typically 0.6–0.8 wt.% oxygen. The determination of the chlorine content of the polymers was carried out by Pascher Mikroanalytisches Laboratorium, Remagen/Germany. Tensile strengths and Young's modulus were measured at room temperature using a tensile test machine type Zwicki 1120 (Zwick/Roell, Ulm/Germany) and a gauge length of 10 mm. The XRD measurements were carried out using a Siemens type D 5005 diffractometer (Cu K α radiation, θ/θ geometry). For the annealing and crystallization experiments, a ASTRO furnace with graphite heaters was used; the annealing was carried out under vacuum. Finally, DTA/TG measurements were performed using a thermal analyser (NETZSCH STA 409 C). Polymers were analysed under argon atmosphere up to 1400 °C; the heating rate was 10 K/min.

3. Results and discussion

3.1. Preparation and properties of the polymers

The polysilanes used in this work were prepared via disproportionation of the disilane fraction purchased from Wacker, Burghausen/Germany. The disilane fraction was purified by distillation, and the portion boiling at 150–154 °C was used. ²⁹Si NMR spectra showed that it consisted of a 1:1 mixture of 1,1,2,2-tetrachlorodimethyldisilane ($\delta(^{29}\text{Si}) = 18.0$ ppm) and 1,1,2-trichlorotrimethyldisilane ($\delta(^{29}\text{Si}) = 15.6$ ppm, 25.0 ppm). The disproportionation was performed by adding 1–2 wt.% of *N*-methylimidazole, which had turned out to be the preferable catalyst in preliminary experiments, and by heating to 220 °C. In some experiments, 10 wt.%

Table 1
Behaviour of polysilane–polycarbosilane copolymers obtained after a thermal treatment of polysilanes

Sample	Thermal treatment (°C/min)	Solubility (solvent)	Fusibility	Cl content (wt.%)
1	–	Readily soluble (toluene)	Melting range 85–110 °C (bulk)	24.4
2	330/60	Readily soluble (CH ₂ Cl ₂)	Melting range 160–180 °C (bulk)	16.7
3	400/60	Readily soluble (CH ₂ Cl ₂)	No melting below 370 °C (bulk)	12.2
4 ^a	–	Readily soluble (toluene)	Melting range 90–120 °C (bulk)	21.7
5 ^a	400/60	Readily soluble (CH ₂ Cl ₂)	No melting below 370 °C (bulk)	10.0
6	350/40	Readily soluble (benzene)	Green fibers partially fused after pyrolysis	Not determined
7	390/3	Readily soluble (benzene)	Green fibers partially fused after pyrolysis	Not determined
8 ^a	400/50	Readily soluble (benzene, toluene)	Green fibers not fused after pyrolysis	10.3

^a Disproportionation was carried out after addition of 10 wt.% of phenyltrichlorosilane to the disilane mixture.

of phenyltrichlorosilane were added before heating. In preliminary experiments, the latter was shown to modify the crosslinking behaviour of the polysilane, leading to a monomodal molecular weight distribution. Additionally, the addition of phenyltrichlorosilane before the disproportionation seems to have an influence on the solubility of the polysilane–polycarbosilane copolymers obtained after a further thermal treatment of the polysilanes (see below).

In a series of experiments, the fusibility and solubility of copolymers, which resulted from the thermal treatment of the polysilanes described above, were investigated. Table 1 gives an overview of the results.

From the data in the table it can be seen that the fusibility of the material is drastically reduced by thermal treatment, whereas its solubility in organic solvents is not significantly influenced in the temperature regime examined. Some samples (not mentioned in the table) were only partially soluble after thermal treatment, but those obtained from polysilanes which resulted from disproportion of the disilane mixture in the presence of phenyltrichlorosilane always remained completely soluble in benzene or toluene. Furthermore, a decrease of the chlorine content from about 20 to 25 wt.% in the polysilane to about 10 wt.% in the copolymer can be observed during thermal treatment, as has already been reported by Babonneau et al.³⁸

The ceramic yield of the copolymers obtained by thermal treating of the polysilanes was examined by DTA/TG measurements (Fig. 1).

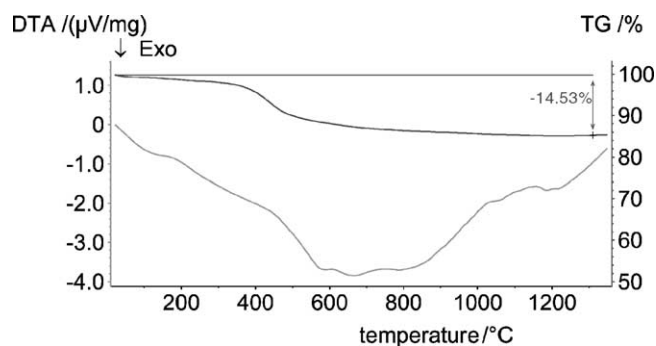


Fig. 1. DTA/TG measurement of a polysilane–polycarbosilane copolymer obtained by the thermal treatment of methylchloropolysilane.

The TG curve shows a strikingly low mass loss, which means a strikingly high ceramic yield of approximately 85 wt.%. Since the material is readily soluble in solvents like toluene and since the viscosity of these solutions can be varied continuously by their polymer content, this high ceramic yield makes the material a promising candidate for matrix infiltrations, too.

3.2. Fiber spinning

Several preliminary experiments were performed to find out a solvent suitable for the dry-spinning process. The copolymers were readily soluble in methylene chloride, but this solvent evaporated too fast during the spinning process, so that no fibers could be obtained. Benzene showed similar results, although in some cases a few fibers could be collected. Toluene showed even better results, allowing continuous fiber spinning during several hours.

A crucial point for fiber spinning via the dry-spinning process is the rheological properties of the copolymer solutions; solutions with viscosities of about 2–5 Pa s turned out to be appropriate. Furthermore, the addition of an organic polymer as a spinning aid was necessary, since otherwise fibers could not be spun under tensile force, resulting in unwanted high diameters and a corresponding brittleness of the green fibers. Thus, the addition of 2 wt.% of polystyrene to solutions

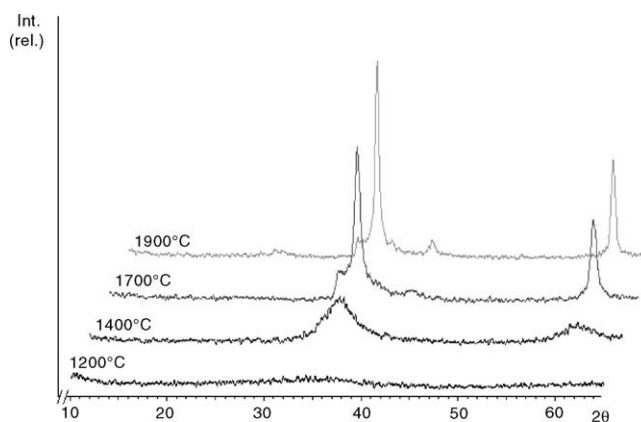


Fig. 2. X-ray powder diagrams of SiC ceramic fibers as pyrolyzed (bottom curve), and heated in a vacuum up to 1400 °C, 1700 °C, and 1900 °C, respectively (upper curves).

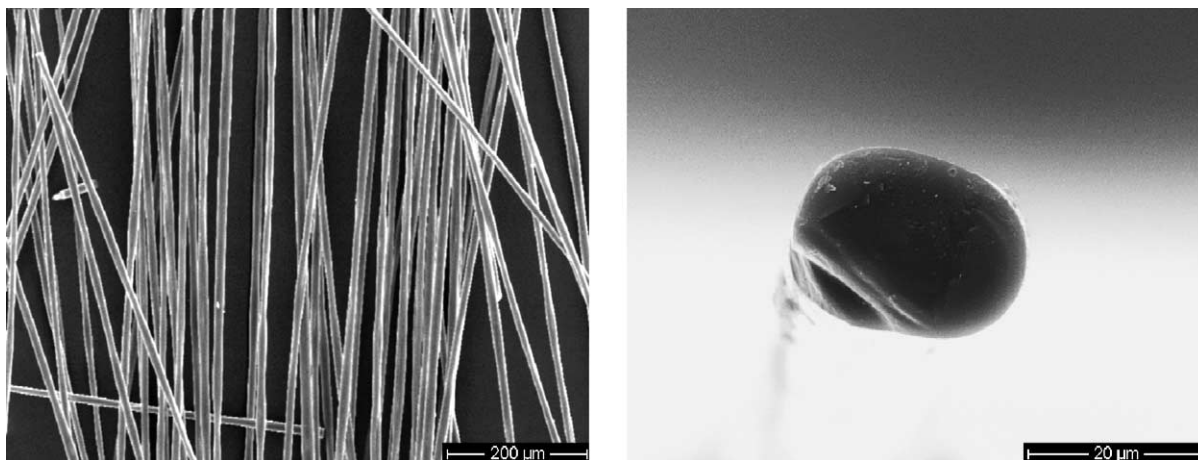


Fig. 3. (Left) SEM image of SiC fibers obtained from a polysilane–polycarbosilane copolymer. (Right) SEM image of a fracture surface of an SiC fiber.

containing 60–70 wt.% of copolymer in toluene led to a material which could be spun continuously into green fibers with diameters of about 30 μm . The further optimization of the spinning conditions, aiming at even lower green-fiber diameters, is in progress.

3.3. Fiber properties

After pyrolysis at 1200 $^{\circ}\text{C}$ under nitrogen, the fibers show room-temperature tensile strengths of up to 800 MPa (diameters of about 25 μm) and Young's moduli of up to 120 GPa; their oxygen content is less than 1 wt.%. Annealing up to 1900 $^{\circ}\text{C}$ leads to an increase of the Young's moduli to values of up to 170 GPa at room temperature without a significant alteration of the tensile strength. In comparison, SiC fibers obtained by Roewer et al. via the melt-spinning of a methylchloropolysilane, the curing of the green fibers under ammonia and the subsequent pyrolysis under argon up to 1200 $^{\circ}\text{C}$ showed tensile strengths of up to 1000 MPa at room temperature; the Young's modulus was estimated to be about 150 GPa.³⁵

During the heating process, the crystallization of β -SiC takes place, as is indicated by the X-ray powder diagrams in Fig. 2. SEM photographs of the fibers (Fig. 3) show that their cross-section is not perfectly circular, but oval or kidney-shaped. Additionally, in most of the fracture surfaces little voids can be seen, which explains the relatively poor tensile strengths. To overcome these disadvantages, further work aiming at an optimization of the spinning, drying step, and the pyrolysis process is in progress.

4. Conclusions

We have developed a new process which leads to SiC ceramic fibers with a low oxygen content, starting from readily available raw materials. The key step in this process consists of a thermal treatment of the initially synthesized polysilane,

leading to an infusible copolymer which is still soluble in organic solvents and thus suitable for e.g. dry-spinning. No curing of the green fibers before pyrolysis is required. Further work, aiming at an optimization of the fiber properties (shape, mechanical strength, microstructure), is in progress.

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