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A Polysilazane Precursor for Si–C–N–O Matrix Composites

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Abstract

This paper reports the ability to use a commercial polysilazane[†] *as matrix precursor for the manufacture of ceramic matrix composites.*

By pyrolysis under nitrogen in the temperature range 1000–1400°C this polysilazane leads to an amorphous silicon carbonitride with a ceramic yield around 65 wt%.

The rheological behaviour and the thermal decomposition of the polysilazane have been studied. Parameters for the impregnation and pyrolysis cycles required by the manufacture of composites are also proposed.

Introduction

For the last 20 years, the organometallic way for the manufacture of ceramic matrix composites has attracted the attention of many industrial and university laboratories.

Indeed, the low temperatures required by precursor pyrolysis limit the risk of the thermal degradation of the reinforcing materials thereby allowing a large panel of potential materials. Low temperatures also induce low energy costs.

Moreover, times required for composites manufacturing (a few days to few weeks depending on the pyrolysis temperature schedules) are significantly shorter than those needed by the Chemical Vapour Infiltration process (many months).

The basic process, using a serial of impregnation and pyrolysis cycles of a fibrous preform by the precursor, appears simple and does not require sophisticated and expensive equipment.[1]

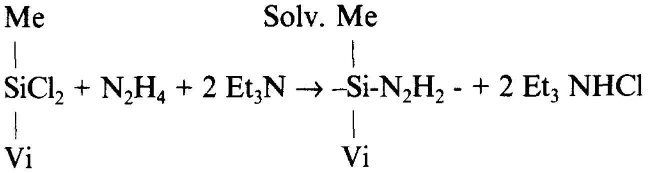
Silicon based ceramics like SiC or Si_3N_4 can be obtained from polycarbonsilanes and polysilazanes.[2] Due to their high mechanical properties and high oxidation resistance, silicon nitride derived materials are interesting as a matrix for thermomechanical composites.[3]

Consequently, research on the synthesis of new polysilazane precursors and the development of a composites manufacturing process using such precursors present a high commercial interest.

1 Synthesis

The synthesis of the polysilazane has already been described in detail by C. Colombier.[4]

PYROFINE PV is a polyvinylsilazane obtained by polymerisation of vinylmethyldichlorosilane with hydrazine in presence of triethylamine.



$$\underset{\text{Vi}}{\underset{|}{\overset{\overset{\text{Me}}{|}}{\text{SiCl}_2}}} + N_2H_4 + 2\,\text{Et}_3\text{N} \xrightarrow{\text{Solv.}} \text{-}\underset{\text{Vi}}{\underset{|}{\overset{\overset{\text{Me}}{|}}{\text{Si}}}}\text{-}N_2H_2\text{ -} + 2\,\text{Et}_3\,\text{NHCl}$$

The choice of hydrazine[††] as nitrogen donor instead of ammonia, which is generally used, results in its higher functionality toward vinylmethyldichlorosilane.

For its part, the solvent is chosen among those in which both polysilazane, chlorosilanes and triethylamine are soluble and $(Et)_3NHCl$ is not.

The monomer condenses to form cyclic structures and by further condensation forms high molecular weight cyclic polymers (Fig. 1).

The typical elemental composition of the precursor is given in Table 1, oxygen originating from the hydrazine used for the synthesis:

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[††] Liquide hydrazine, bp: 130°C.

Table 1.

	Si	*C*	*N*	*O*	*H*
wt%	31·5	37·2	20·3	3·2	7·8
at%	8·2	22·7	10·5	1·4	57·2

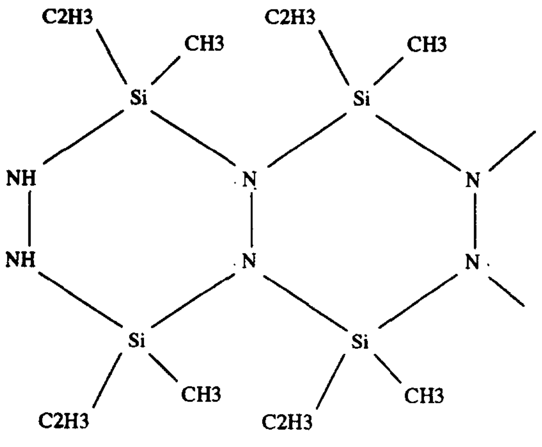

Fig. 1. Structure of the polysilazane.

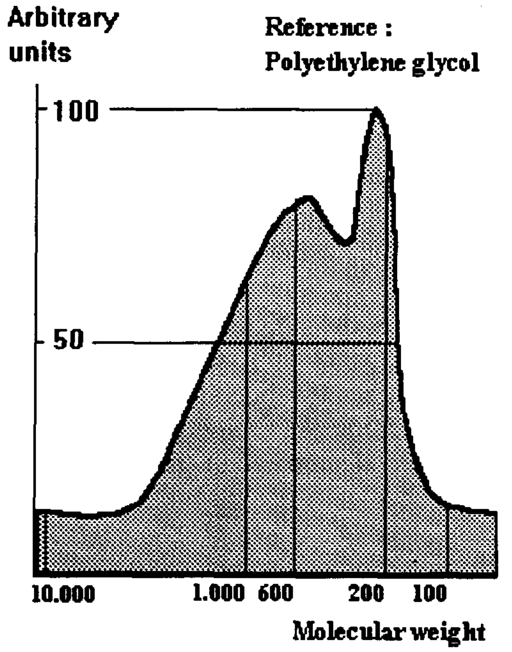

Fig. 2. Molecular weight distribution of the polysilazane.

The gel permeation chromatography shows the large molecular weight distribution of the precursor (Fig. 2). *M* varies from 0 up to more than 10 000 with a maximum in number between 200 and 1200 corresponding respectively to 1–6 elemental cycles. The average molecular weight in number is 500. A large amount of low molecular weight oligomers ($M < 100$) is also evident.

2 Rheology

At room temperature, the polysilazane is a high viscous liquid with a density close to 1. Upon heating up to 150°C its viscosity decreases with the increase in temperature (Fig. 3) and remains stable during numerous hours (Fig. 4).

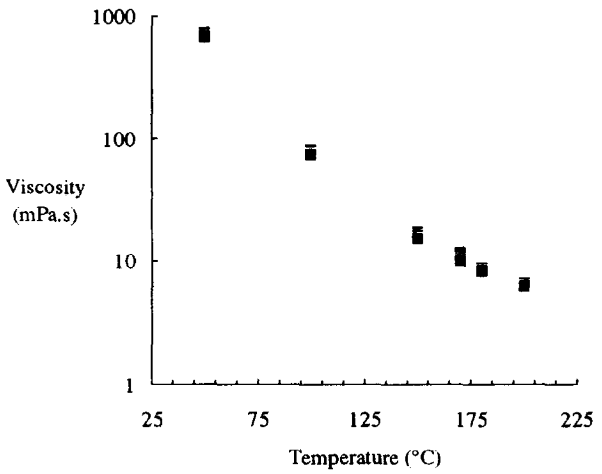

Fig. 3. Variation of the viscosity of the polysilazane versus temperature.

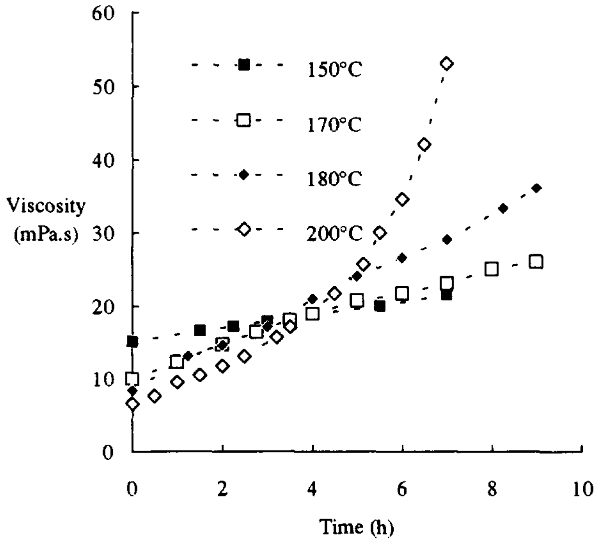

Fig. 4. Variation of the viscosity of the polysilazane versus time at different temperatures.

Above 150°C and up to 220°C, the viscosity still decreases versus temperature but increases quickly versus time. The low molecular weight oligomers may be evaporated or may condense to form longer chains. That increases the average molecular weight of the precursor and consequently, explains the variation of the viscosity versus time.

3 Evolution of the Polysilazane Versus Temperature

3.1 From room temperature up to 300°C

Below 150°C, no weight loss is observed on the TGA curve (Fig. 5, part I). Between 150 and 300°C a 15% weight loss is measured (Fig. 5, part II). The mass spectrometry coupled with the TGA indicates an ammonia release (Fig. 6) which could correspond to the condensation reaction:

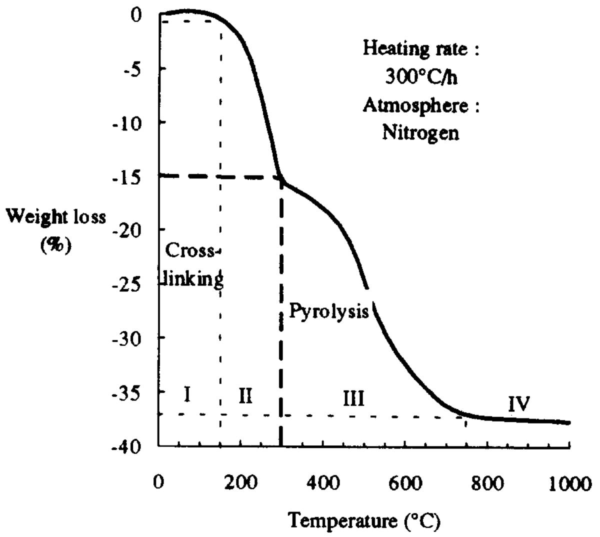

Fig. 5. TGA curve of the polysilazane.

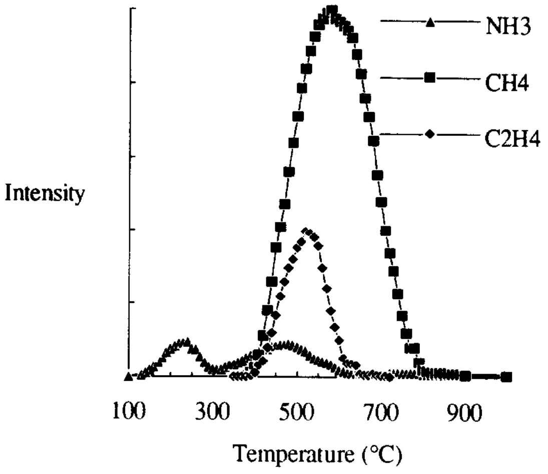

Fig. 6. Mass spectrometry associated to the TGA (Fig. 5).

$$2 \equiv \text{Di-NH-NH}_2 \rightarrow \equiv \text{Si-NH-NH-Si} \equiv + \text{N}_2\text{H}_4$$

Above 250°C, the hydrazine released may decompose to ammonia and nitrogen with a strong exothermic reaction (–336 kJ/mol):

$$3\text{N}_2\text{H}_4 \rightarrow \text{N}_2 + 4\ \text{NH}_3$$

The titrage by reaction in H_2SO_4 of the ammonia generated up to 300°C explains only 1–2% of the 15% weight loss measured by TGA. The evaporation of the light oligomers can explain the bulk of the weight loss. These oligomers are not observed by the mass spectrometry because they condense in the apparatus before the detection.

Between 220 and 300°C the precursor is progressively transformed from a soluble (in toluene) liquid into an unmeltable and insoluble solid.

Table 2.

Heating rate (°C/h)	*Temperatures (°C)*	*Holding time (h)*
100	20–130	0
5	130–*T*°C	1

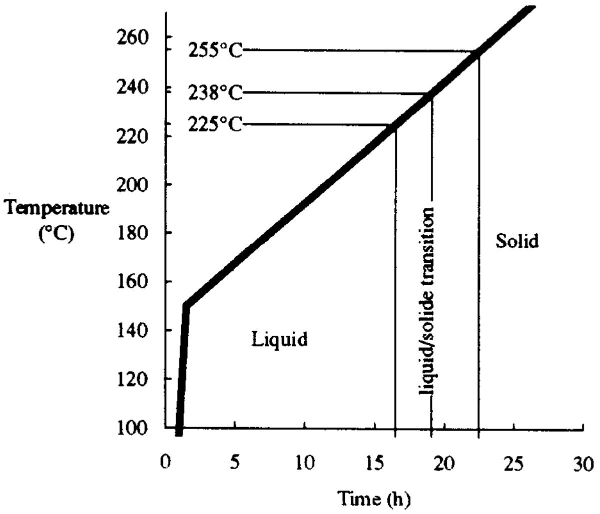

Fig. 7. Temperature range of the precursor cross-linking.

That is evidenced by successive heat treatments on the precursor using the following temperature schedule (Fig. 7 and Table 2):

T = 225°C; the product obtained is a high viscous liquid soluble in toluene.

T = 238°C; the product is solid, soluble in toluene, its melting point is about 100°C. Bubbles are observed on the surface of the sample.

T = 255°C; the product is solid, unmeltable and insoluble. Numerous bubbles are observed in the cross-section of the sample.

The ^{29}Si solid NMR confirms that the cross-linking is due to the opening of the vinyl groups.[5]

$$\equiv\text{Si–CH=CH}_2 \text{ transforms to } \equiv\text{Si–CH–CH}_2$$

The liquid to solid conversion corresponding to the vinylic cross-linking combined with the generation of gases due to the condensation reaction and the oligomers evaporation, which leads to the

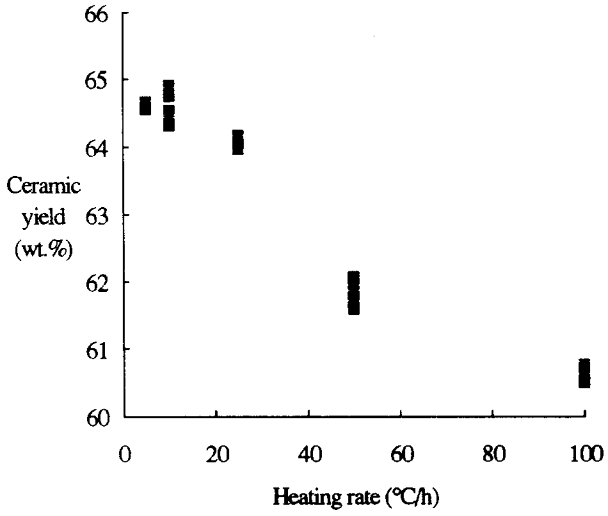

Fig. 8. Variation of ceramic yield at 1000°C versus the heating rate used during the cross-linking (temperature range 130–300°C) the heating rate used from 300–1000°C being 1000°C/h.

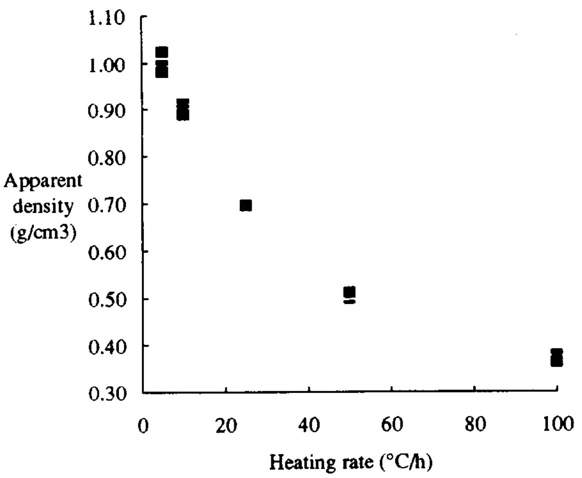

Fig. 9. Apparent density of the ceramic obtained after pyrolysis at 1000°C versus the heating rate used during the cross-linking (temperature range 130–300°C) the heating rate used from 300–1000°C being 100°C/h.

formation of foam, and after pyrolysis to high porous volume ceramics.

As it has previously been shown, the major part of the gas generated arises from the evaporation of the low molecular weight oligomers. This evaporation can be controlled by the heating rate used before and total solidification of the precursor. Indeed, using various heating rates between 130 and 300°C and then achieving the pyrolysis at 100°C/h between 300 and 1000°C we noted that the ceramic yield is higher, when the heating rate used is low.[6] (Fig. 8).

The decrease of the gas released during the solid liquid transition also reduces the foaming and then increases the apparent density of the ceramic residue (Fig. 9).

3.2 Above 300°C

Above 300°C the mineralisation starts. The weight loss between 300 and 800°C is 20–25% (Fig. 5, part III) and the gas release is maximum around 500°C. In the early stage of this step, the ammonia release remains high (Fig. 6) and could be explained by transamination reactions.[5,6]

$$\equiv\text{Si–NH–NH–Si}\equiv + \equiv\text{Si–H} \rightarrow \equiv\underset{\substack{|\\ \text{Si}\equiv}}{\text{Si–N–Si}}\equiv + \text{NH}_3$$

Up to 600°C mainly methane but also methylene, propene and other unsaturated hydrocarbons are generated (Fig. 6).

Methane may originate from the decomposition of the methyl groups.[6]

$$\equiv\text{Si–CH}_3 \rightarrow \equiv\text{Si}^* + {}^*\text{CH}_3$$

$${}^*\text{CH}_3 \xrightarrow{\text{H abstraction}} \text{CH}_4$$

The unsaturated hydrocarbon released could arise from the decomposition of isolated vinyl groups which are not in a position to react with another vinyl group.

$$\equiv\text{Si–CH=CH}_2 \rightarrow \equiv\text{Si}^* + {}^*\text{CH=CH}_2$$

The $^*CH=CH_2$ groups may react with $^*H$, $^*CH_3$ or with another $^*CH=CH_2$:

$${}^*\text{CH=CH}_2 + {}^*\text{H} \rightarrow \text{C}_2\text{H}_4$$

$${}^*\text{CH=CH}_2 + {}^*\text{CH}_3 \rightarrow \text{C}_3\text{H}_6$$

$${}^*\text{CH=CH}_2 + {}^*\text{CH=CH}_2 \rightarrow \text{C}_4\text{H}_6$$

Above 600°C and up to 800°C only methane is detected. Hydrogen may also be generated from the cleavage of the Si–H, N–H bonds but not detected by mass spectrometry. At higher temperatures the cleavage of the Si–C bonds leads to the formation of Si–N and graphite which is evidenced by ^{13}C solid state NMR after heat treatment at 1000°C. The typical elemental composition of the ceramic obtained after pyrolysis at 1000°C is given in Table 3:

Table 3.

	Si	*C*	*N*	*O*
at%	30·0	34·7	27·1	8·2
wt%	47·5	23·6	21·5	7·4

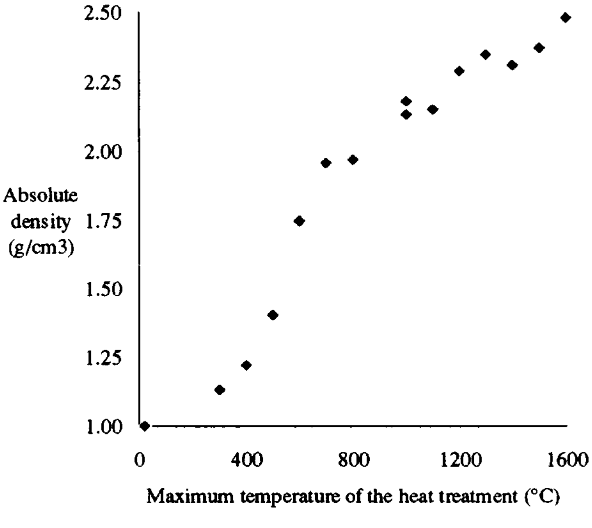

Fig. 10. Absolute density of the residue obtained after heat treatment under nitrogen at various temperatures.

Table 4.

Highest temp. (°C)	*Absolute density (g/cm³)*
1000	2·13
1100	2·18
1200	2·27
1300	2·31
1400	2·35
1500	2·38
1600	2·48

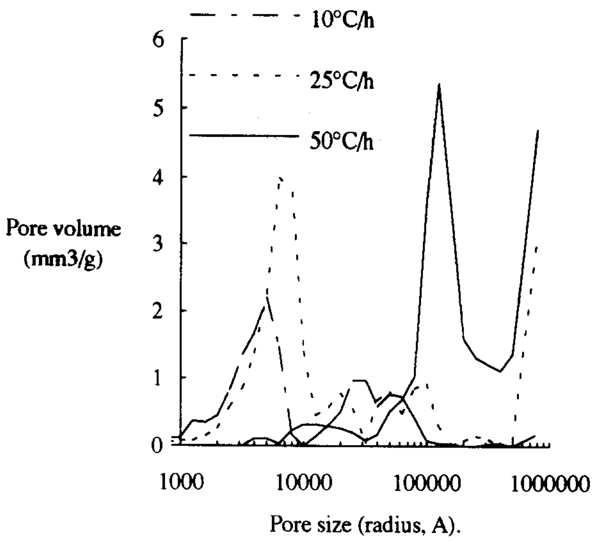

Fig. 11. Pore size distribution in the ceramic samples versus the heating rate between 300 and 1000°C.

The true density of the ceramic has been determined by He picnometry on milled samples. The densities measured depending on the maximum temperature of the pyrolysis as shown (Fig. 10 and Table 4).

3.3 Crystalline structure

Up to 1400°C the ceramic residue remains almost totally amorphous. Only a low signal corresponding to SiO_2 is detected by X-ray diffraction.

Above this temperature, peaks corresponding to α SiC and α Si_3N_4 appear on the graph.[7] It has already been shown that the crystallisation corresponds to the formation of whiskers and of a coating at the pores' surfaces. This leads also to a decrease in the mechanical properties of the ceramic.[8]

3.4 Influence of the heating rate during the mineralisation

Using a specific process for the manufacture of monolithic bodies,[8] ceramic samples were realised using various heating rates (50, 25 and 10°C/h) during the mineralisation step.

After pyrolysis at 1000°C, the true and apparent densities of the samples are similar; 1·91 and 2·15 respectively and correspond to 12–13% porosity. On the other hand, the pore size distribution determined by mercury porosimetry is significantly different versus the heating rate used (Fig. 11). A low heat rate (10°C/h) leads to pores having 2–10 μm radius whereas a faster heating rate (50°C/h) creates pores having more than 20 μm radius.

Moreover, the pores studied by mercury porosimetry correspond to the opened porosity. The porous volume measured on the samples pyrolysed at 10°C/h is significantly lower than that of the samples pyrolysed at 50°C/h. The total porous volume being the same, the ratio open porosity/closed porosity increases as the heating rate is high.

Conclusion

The polysilazane studied appears as an interesting precursor for the manufacture of ceramic matrix composites. Indeed its low viscosity, about 10 mPas at 150°C, and its high stability versus time at this temperature make it particularly suitable for the infiltration of fibrous or particulate preforms.

Moreover, the ceramic yield is high, about 60–65 wt% (About 30 vol%) after pyrolysis at 1000°C, then the number of impregnation and pyrolysis cycles required to obtain low porosity composites would be low. The low true density of the ceramic (2·13 g/cm^3 after pyrolysis at 1000°C) is also interesting.

However, a gas generation, mainly due to the evaporation of low molecular weight oligomers, and taking place simultaneously to the precursor cross-linking leads to the formation of a foam and consequently to a high porous volume in the ceramic after pyrolysis. A low heating rate, 5°C/h, between 130°C–300°C reduces the evaporation of the low molecular weight oligomers and then increases the ceramic yield and the apparent density of the ceramic. Nevertheless in the best case the porosity remains higher than 50%.

Above 300°C the heating rate does not influence the porosity amount in the ceramic but has significant consequences on the pore size distribution. A low heating rate leads to finer pores but creates more closed porosity than a higher one. Therefore, as successive impregnation and pyrolysis cycles will be required, a mean heating rate, about 25°C/h would be used. The ceramic residue remains amorphous up to a pyrolysis temperature of 1400°C. Above this temperature the αSiC and αSi_3N_4 crystallisation leads to a decrease in the mechanical properties of the ceramic.

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