

Pyrolysis of Polyvinylsilazane Precursors to Silicon Carbonitride

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Abstract

The pyrolysis of liquid or solid polyvinylsilazanes, cross-linked according to four different routes, was studied in the 20–1400°C temperature range. The similar behaviour and the high ceramic yields ($\approx 85\%$) are related to the reactivity of the functional groups ($-\text{CH}=\text{CH}_2$, $\text{Si}-\text{H}$, $\text{N}-\text{H}$) which lead to highly cross-linked solids before the mineralization step. The major gases evolved above 450°C are hydrogen, methane and ethylene. During the thermal treatment $\text{Si}-\text{N}$ bonds are unaffected. The silicon carbonitride samples are dense and amorphous up to 1400°C. The thermal stability of the microtexture is due to the high carbon content.

Das Pyrolyseverhalten von vier durch unterschiedliche Reaktionsverläufe vernetzten flüssigen oder festen Polyvinylsilazanen wurde im Temperaturbereich von 20–1400°C untersucht. Das ähnliche Verhalten und der hohe Keramikanteil ($\approx 85\%$) werden auf die Reaktivität der funktionellen Gruppen ($-\text{CH}=\text{CH}_2$, $\text{Si}-\text{H}$, $\text{N}-\text{H}$) zurückgeführt, die bereits vor der Mineralisation zu hochvernetzten Polymeren führen. Über 450°C entweichen vor allem Wasserstoff, Methan und Ethen. Die Wärmebehandlung beeinflusst die $\text{Si}-\text{N}$ -Bindungen nicht. Die Siliziumcarbonitridproben sind dicht und bleiben bis zu 1400°C amorph. Die Temperaturbeständigkeit des Materials wird auf den hohen Kohlenstoffgehalt zurückgeführt.

Des polyvinylsilazanes liquides ou solides obtenus

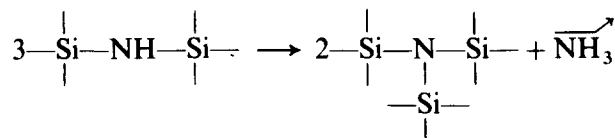
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selon quatre voies différentes ont été pyrolysés sous azote dans l'intervalle 20–1400°C. Les comportements voisins et les rendements céramiques élevés ($\approx 85\%$) s'expliquent par la réactivité des groupes fonctionnels ($-\text{CH}=\text{CH}_2$, $\text{Si}-\text{H}$ et $\text{N}-\text{H}$) qui conduisent à des polymères fortement réticulés avant l'étape de minéralisation. Les principales espèces volatiles qui se dégagent au-dessus de 450°C sont l'hydrogène, la méthane et l'éthylène. Les liaisons $\text{Si}-\text{N}$ ne sont pas affectées par le traitement thermique. Les carbonitrides de silicium sont compacts et amorphes jusqu'à 1400°C. Leur stabilité thermique est liée à la présence d'une teneur élevée en carbone.

1 Introduction

The increasing needs of materials with good mechanical properties at high temperature explain the growing interest in high performance ceramics. In this area the polymer pyrolysis route is promising.¹ The main advantage of polymers as preceramic materials arises from the possibility of obtaining various shapes which are difficult to achieve by other processes. Thus ceramic fibres, thin films or coatings are fabricated by conventional plastic processing of the polymer, followed by a thermal treatment.² Polymers may also be used as binders for sintering powders³ and for infiltration of porous ceramic bodies. One of the limitations of the process is the loss of volatile organometallic species, frequently observed during pyrolysis, which may drastically lower the ceramic yield.^{1,4} This loss

The transamination pathway which leads to trisilylated nitrogen atoms, with a release of ammonia, occurs only to a small extent:



The main difference between the four samples P_1 – P_{IV} is their cross-linking degree. When the OVSZ is reacted neat, the cross-linking degree is higher than in solution and resins are readily obtained. The hydrosilylation rate is faster when Pt catalyst is used. Thus, the cross-linking degree for the different samples are in the order $P_1 < P_{II} < P_{III} < P_{IV}$. However, a large amount of Si—H, —CH=CH₂ and N—H functions are preserved in all the samples, as indicated by IR spectroscopy.

3 Experimental Procedure

The thermal decomposition in flowing nitrogen or argon was investigated by using a thermogravimetric analyser (Netzsch STA 409) interfaced with a quadrupole mass spectrometer (Kenos KSM88, ionization energy 70 eV). During the pyrolysis, scans from 2 to 150 a.m.u. were collected every 30 s and stored. This equipment (TGA/MS) allows the identification of the different gases evolved during the pyrolysis, and the plotting of the signal of characteristic ions as a function of the temperature, along with the TGA curve. Samples were heated (20–1400°C) in an alumina crucible with different heating rates (50, 150, 600 and 750°C/h). The pyrolysis products were characterized by elemental analysis (Service Central d'Analyses du CNRS), IR spectroscopy (FTIR Nicolet 5 DX) and X-ray diffractometry (Philips PW 1730). Microstructural features were examined with scanning electron microscopy (Jeol JSM 35) and the specific surface area by the BET method (Micromeritics 2205).

4 Results

4.1 Thermal decomposition: TGA and mass spectrometry

Under pyrolysis conditions the four samples exhibit similar behaviour, as shown in Table 4. It is noteworthy that whatever the cross-linking degree of the precursor and the heating rate, the ceramic yields are identical. Isothermal experiments indicate that the decomposition is very slow. For example, at

Table 4. Ceramic yields (wt%) at 1200°C and N₂ (1 atm)

Heating rate (°C/h)	P_I	P_{II}	P_{III}	P_{IV}
50	84	86	83	85
150	84	86	—	—
750	85	86	84	85

600°C decomposition of the sample necessitates at least 24 h to go to completion.

The TGA curves for the four samples have the same shape. The weight loss for the precursor P_1 is shown in Fig. 1. The analysis of the gases evolved allows a more accurate description of the thermolysis process (Fig. 1).

Four stages may be distinguished:

- From 130 to 250°C a weight loss lower than 3% is detected, which may be due to distillation of oligosilazanes (not detected) and/or to evaporation of residual solvent.
- In the 250–450°C interval a very small amount of ammonia ($m/z = 16, 17$) is detected; towards 350°C a large hydrogen release ($m/z = 2$) starts. The corresponding weight loss is lower than 1%.
- An important weight loss is recorded between 450 and 750°C, which corresponds mainly to a large release of methane ($m/z = 15, 16$) and to the continuation of hydrogen escape. Small amounts of other hydrocarbons such as ethylene ($m/z = 27$) and propene ($m/z = 41$) are also observed.
- Between 750 and 1200°C hydrogen is the only gas detected. The corresponding weight loss is less than 1.5%.

4.2 Pyrolysis products: composition, IR and XRD analysis, morphology

The sample P_1 was heated at various temperatures between 20 and 1400°C, and the pyrolysis products

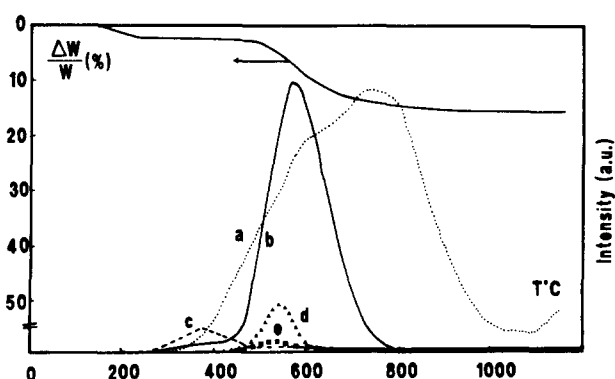


Fig. 1. Weight loss and mass spectrometric curves versus pyrolysis temperature: a, $m/z = 2$; b, $m/z = 16$; c, $m/z = 17$; d, $m/z = 27$; e, $m/z = 41$; conditions: 20–1150°C, heating rate 10°C/min, in argon.

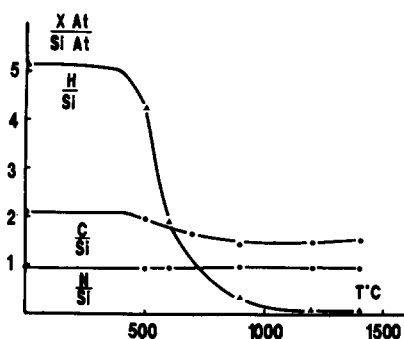


Fig. 2. Chemical composition of pyrolysis products at various temperatures.

were characterized by elemental analysis and infrared spectroscopy. Up to 500°C there is no important modification of the residue composition, except for the hydrogen content, which at 500°C is about 15% lower than the theoretical one for OVSZ (Fig. 2). The main changes occur between 500 and 800°C, with a loss of hydrogen and carbon. At 850°C the release of hydrocarbons is complete; in contrast, the hydrogen loss goes on up to 1200°C.

Figure 3(a) and (b) display the IR spectra of P_I and those of products obtained by heating P_I from 200 to 1200°C. At 200°C the most striking feature is the growth of bands around 2900 cm^{-1} (aliphatic C—H stretching), which is correlated with the decrease in the band intensities of the vinyl groups at 3050–3010, 1592, 1403 and 1269 cm^{-1} . In this temperature range the Si—H stretching band at 2130 cm^{-1} appears less modified. These structural changes are connected with a drastic increase of the cross-linking degree: when a liquid sample (P_{II}) is heated for 10 min at 200°C it converts into a glassy solid. Between 300 and 500°C the peaks arising from N—H, Si—H and vinyl groups are markedly reduced. At a reaction temperature of 1200°C the residual Si—H and vinyl groups as well as the aliphatic C—H are eliminated. The spectra shows only broad absorption bands arising from Si—N and Si—C.

High-temperature applications for materials obtained by polymer pyrolysis need studies on their thermal stability. Polyvinylsilazanes were heated under nitrogen up to 1400°C. Results summarized in Table 5 and in Fig. 4 show that the silicon carbonitride obtained is stable and amorphous. After an annealing time of 12 h, the formation of α - Si_3N_4 is indicated by X-ray diffraction. As for other

Table 5. Isothermal weight loss (%) at 1400°C and N_2 (1 atm)

Precursors	Weight loss ($\Delta W/W$, %)	
	12 h	24 h
P_I	5	6
P_{II}	4	8.8

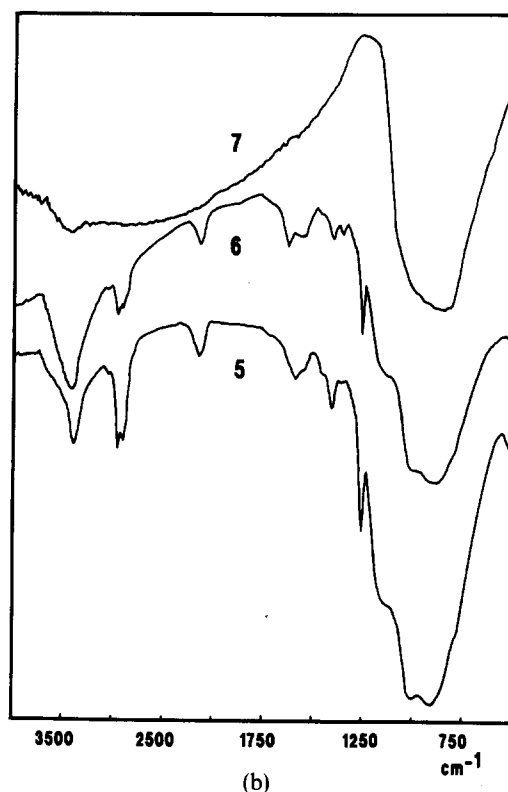
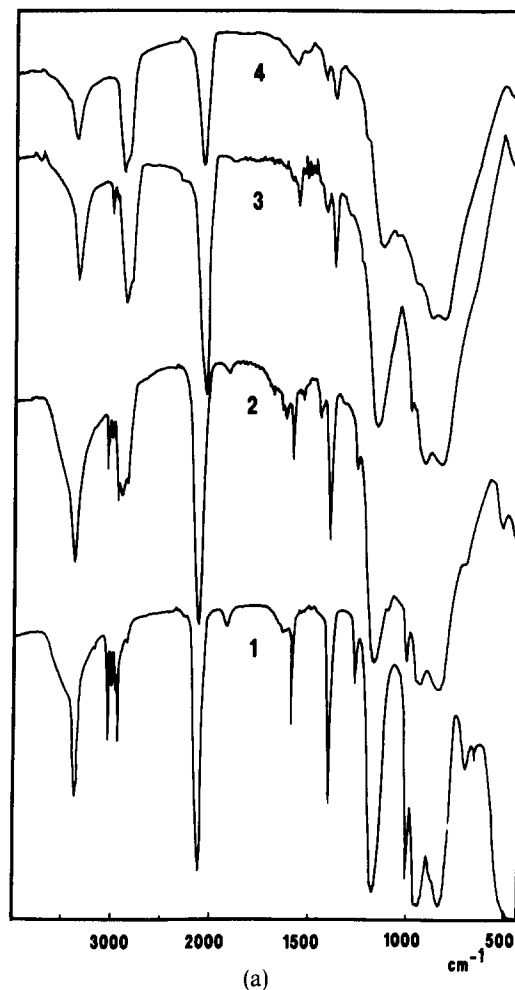


Fig. 3. IR spectra of P_I (1), and of products heat treated at 200°C (2), 300°C (3), 400°C (4), 500°C (5), 650°C (6) and 1200°C (7).

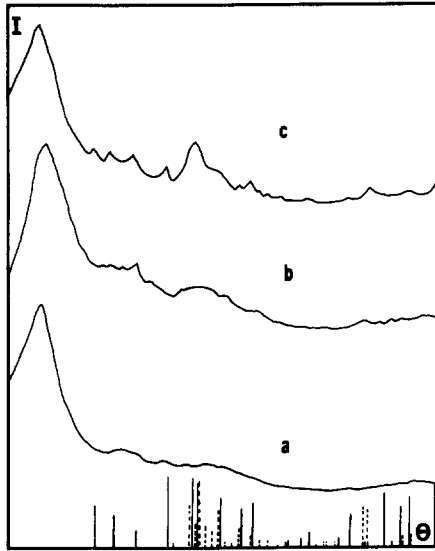
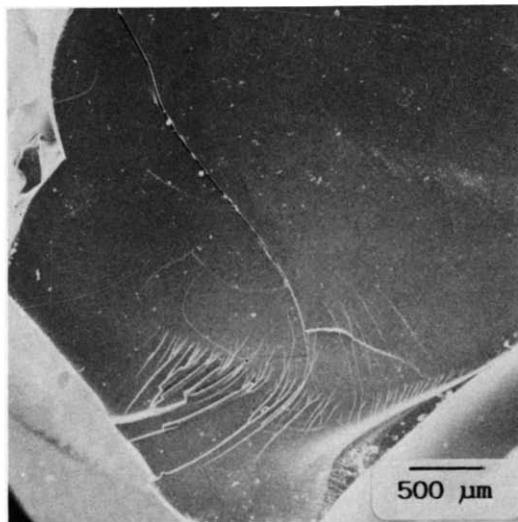


Fig. 4. X-Ray diffraction patterns of P_1 heat treated in nitrogen at 1400°C : a, 1 h; b, 12 h; c, 24 h; —, $\alpha\text{-Si}_3\text{N}_4$; ---, $\alpha\text{-SiC}$.

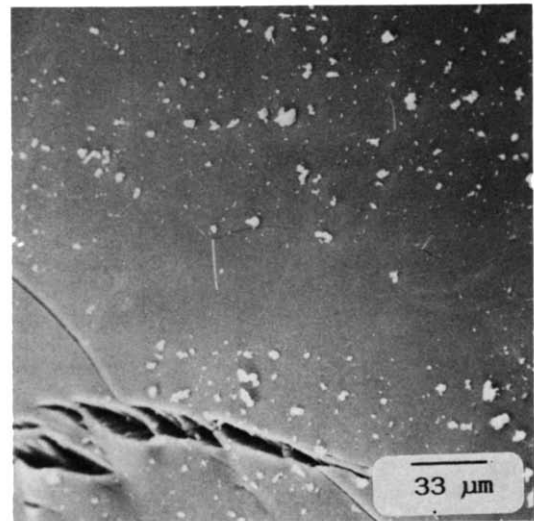
precursors, the crystallization seems to be connected to the gas release.¹²

The silicon carbonitride samples were examined by SEM in order to obtain information on changes during pyrolysis. The texture depends on the heat treatment conditions.¹³ The ceramics are compact with some heterogeneities for a slow heating rate (Fig. 5). They retain their shape but some microcracks due to the stresses induced by the volume decrease are observed. With a fast heating rate the gas release creates porosity and microcracks without a bloating of the material. The reactions which occur at low temperature ($200\text{--}300^\circ\text{C}$) restrict the distillation of oligomers.

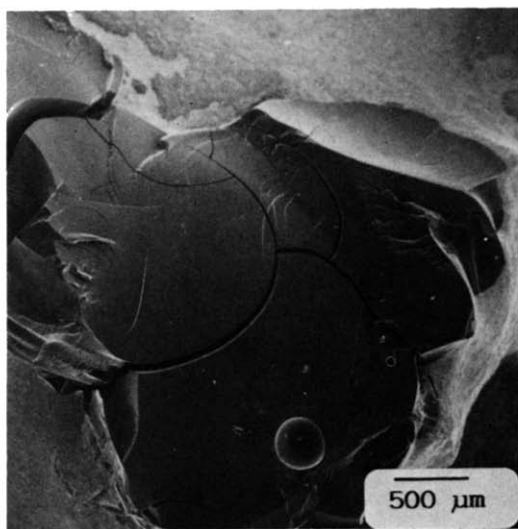
Specific surface areas were determined by argon adsorption using the BET technique. Pyrolysis products heated up to 1400°C are dense and the specific surface area is too low to be measured. Open



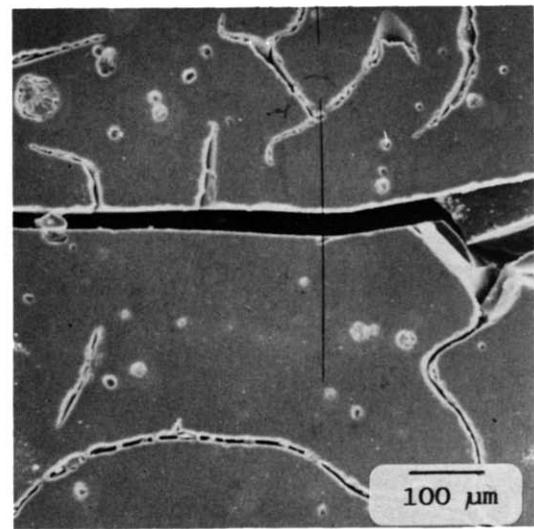
(a)



(b)



(c)



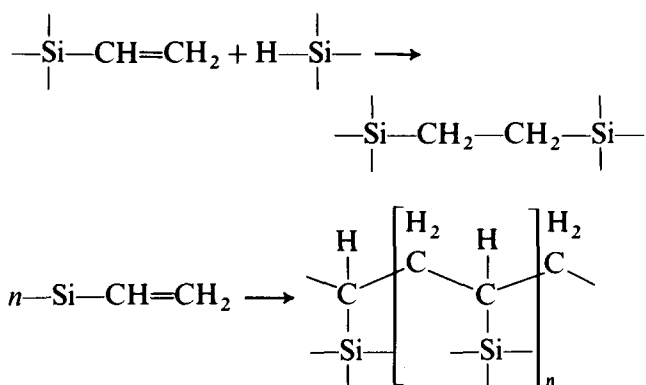
(d)

Fig. 5. SEM micrographs of silicon carbonitride samples heat treated in nitrogen at 1400°C ; heating rate: a and b, $50^\circ\text{C}/\text{h}$; c and d $750^\circ\text{C}/\text{h}$.

porosity is formed during annealing at 1400°C, when the residue starts to crystallize.

4.3 Discussion

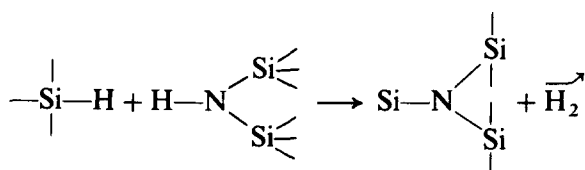
Due to the presence of the three functional groups (Si—H, vinyl and N—H) OVSZ is easily cross-linked to liquid or solid precursors. It may be noted that the heating rate and the molecular weight distribution have no influence on the conversion into silicon carbonitride. Ceramic yields are high ($\approx 85\%$) for the liquids as well as for the solids precursors. The exothermic peak characterized on DTA curves between 130 and 250°C indicates the occurrence of a reaction. The polysilazanes are solid and brittle. In this temperature range IR spectra show a decrease of vinyl absorption bands and formation of aliphatic C—H. The other functional groups are less modified. These changes may be explained by two reactions where the vinyl groups are involved:



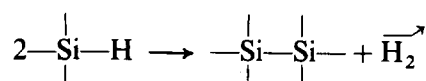
It seems that the hydrosilylation rate is slower than that of the polyaddition reaction, insofar as the intensity of Si—H bands appears less modified.

These cross-linking reactions, occurring at the beginning of the pyrolysis process, eliminate the structural differences between the four samples. This explains their similar behaviour during mineralization and the high ceramic yields observed whatever the initial cross-linking degree.

As shown by mass spectrometry, hydrogen evolves at lower temperature ($T \approx 330^\circ\text{C}$) than for the pyrolysis of polycarbosilanes.^{14,15} This release may result either from dehydrogenation between Si—H and N—H groups:

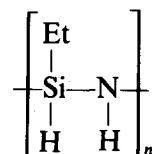


or from reactions between two Si—H groups:



However, Si—Si bonds formation from Si—H dehydrogenation has not been shown for polycarbosilanes. The first mechanism is consistent with the decrease of IR absorptions of Si—H and N—H bonds and leads to the formation of very stable trisilylated nitrogen atoms. All these reactions induce the formation of a rigid tridimensional network with a slight weight loss.

The mineralization starts above 450°C with the cleavage of Si—C, C—C, C—H and N—H bonds, and the diffusion of gaseous species (H_2 , CH_4 , C_2H_4). Traces of hydrogen are detected up to 1200°C. The environment of silicon in the silazane is progressively modified. Mass spectrometry results and elementary analysis show that during the pyrolysis the Si—N bonds are very stable. The molar composition of P_1 at 1400°C is $\text{SiN}_{0.98}\text{C}_{1.47}\text{O}_{0.06}\text{H}_{0.06}$, to be compared with the theoretical composition of the starting OVSZ: SiNC_2H_5 . Therefore this silicon carbonitride ($\text{SiN}_{0.98}\text{C}_{0.22}\text{O}_{0.06}\text{H}_{0.06}1.25\text{C}$) is composed of carbon-free and Si—N—Si, Si—C—Si (Si—O—Si traces) bonds which build up a structure of randomly distributed tetrahedra with mixed compositions $\text{SiC}_x\text{N}_{4-x}$. Assuming that the pyrolysis product P_1 is completely crystallized and is a mixture of Si_3N_4 , SiO_2 , SiC and C, the apparent composition (wt%) would be 58% Si_3N_4 , 3.1% SiO_2 , 15.9% SiC and 23% C. This high carbon content has to be related to the cross-linking reaction involving the vinyl groups. In the case of



precursors the ethyl groups are not efficient to cross-link the structure.¹⁶ The apparent carbon content of the ceramic is lower.

IR spectra and X-ray patterns show that the carbonitride is amorphous at 1200°C. Crystallization is very slow, even at 1400°C; $\alpha\text{-Si}_3\text{N}_4$ and $\alpha\text{-SiC}$ were detected only after long heat treatments. This atomic rearrangement is observed at higher temperature than for ceramics resulting from the pyrolysis of polycarbosilanes,^{14,17} or from silicon diimide $\text{Si}(\text{NH})_2$.¹⁸ The silicon carbonitrides obtained from polymethylsilazanes $[\text{SiMeH}(\text{NH})]_n$ ⁷ and $[\text{SiMe}_2(\text{NH})]_n$ ¹³ also remains amorphous up to 1400°C. All these results suggest that at 1200–1400°C ceramics obtained from polycarbosilazanes consist of various $\text{SiC}_x\text{N}_{4-x}$ tetrahedra and free carbon which hinder the crystallization of Si_3N_4 and SiC.

5 Conclusion

Polyvinylsilazanes lead after pyrolysis to silicon carbonitride with a high ceramic yield ($\approx 85\%$) whatever the initial cross-linking degree. This behaviour is explained by the occurrence at low temperature ($\approx 200^\circ\text{C}$) of a polyaddition of vinyl groups and a hydrosilylation reaction which induce the formation of highly cross-linked, hard and brittle solids.

During the mineralization step the evolution of gaseous species (H_2 , CH_4 , C_2H_4 , etc.) corresponds to bond cleavage, but the Si—N bonds are unaffected. Owing to the stable framework formed, weight loss is reduced and the samples retain their shape. On the other hand, the final carbon content is high in the silicon carbonitride ($\text{SiN}_{0.96}\text{C}_{1.47}\text{O}_{0.06}$). By comparison with other precursors the ceramic obtained remains amorphous at a higher temperature.

These polyvinylsilazanes seem promising for matrix applications or as binders. It is easy to control the cross-linking degree to obtain viscous liquids for the impregnation of fibre preforms. Then a heat treatment at 200°C will complete the cross-linking prior to pyrolysis, which will reduce the outgassing and the problems of bloating or delamination.

Acknowledgements

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