

Comparison of Two Processes for Manufacturing Ceramic Matrix Composites from Organometallic Precursors

Maurice F. Gonon* and Stuart Hampshire

Materials Ireland Research Centre, University of Limerick, Limerick, Ireland

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Abstract

A commercial polysilazane is used as a silicon carbonitride matrix precursor for the manufacture of ceramic matrix composites using bi-directional SiC Nicalon fabrics as reinforcing material. The objective is to develop a simple and fast process leading to materials able to compete with SiC/C/SiC composites obtained by the Chemical Vapour Infiltration (CVI) route. Two processes are investigated: (1) a 'conventional' process using the densification of a SiC fibre preform by several cycles of impregnation of the preform with the polymer followed by pyrolysis and (2) a 'modified' process consisting in a powder filling of the fibre preform prior to the precursor impregnation and pyrolysis. This paper describes the different steps of both processes. The materials obtained are characterised in terms of their porosity, microstructure and mechanical properties. © 1999 Elsevier Science Limited. All rights reserved

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1 Introduction

The use of organometallic precursors to manufacture ceramic fibre reinforced composites (e.g. SiC/C/SiC or C/SiC) appears as a very attractive alternative way to the CVI route. Indeed, the CVI route, which leads to materials with high mechanical properties, needs a very long manufacturing time, sophisticated equipment and is therefore very expensive.^{1,2} On the contrary, a previous work has shown that composites may easily be obtained from a polysilazane precursor.^{2,3}

*To whom correspondence should be addressed at: Faculté Polytechnique de Mons, Service de Science des Matériaux, Rue de l'Épargne, 56, B-7000 Mons, Belgium.

The organometallic route consists in filling a fibre preform by operating successive impregnations of the preform with a precursor, followed by the pyrolysis of the precursor. However, according to the high porosity of the initial fibre preform (typically around 60%) and the low ceramic yield of the precursor (≈ 30 vol%), a high number of impregnation/pyrolysis cycles is required to densify the composites (up to nine cycles).

Despite of this high number of cycles, the time required to manufacture the composites is already significantly shorter in comparison with the CVI route (a couple of weeks instead of several months). However in order to reduce this time and also to decrease the amount of precursor used, the spaces existing between each ply of fabric of the fibre preform can be filled with submicron ceramic powder prior to the first impregnation with the precursor. Assuming that approximately 40% of the initial porosity can be filled with the powder, then only three to four impregnation/pyrolysis cycles would be required to complete the densification.

2 Experimental

2.1 Manufacture of the composites

Nicalon silicon carbide fabrics NL 202 S8, supplied by Nippon Carbon (J), are used as reinforcing material. The polysilazane precursor, Pyrofine PV, is supplied by the company Elf-Atochem (F).⁴

Due to its low and stable viscosity at a temperature of 150°C the precursor can easily impregnate fibre preforms.⁵ By pyrolysis in a nitrogen atmosphere in the temperature range 1000–1400°C, the polysilazane decomposes into an amorphous silicon carbonitride compound with a ceramic yield of 65 wt% (30 vol%). The maximum in density and mechanical properties is obtained after pyrolysis at 1400°C.⁶ However, to

avoid the thermal degradation of the fibres the pyrolysis must be operated at a maximum temperatures of 1200°C.

It is now well known that the mechanical behaviour of fibre reinforced composites dramatically depends on the characteristics of the interface between the fibres and the matrix.⁷ A weak interface leads to energy dissipative mechanics such as fibre pullout and debonding which increase the energy required for the propagation of the cracks and leads to a high toughness. Therefore the fibres are coated by CVD with a few tenths of a micron thick carbon layer.⁸

2.1.1 'Conventional' composites

According to the desired fibre fraction, eight to 10 plies of fabric (65×120 mm), are cut, carbon coated and placed into a stainless steel die as shown in Fig. 1. The die and the fabrics are heated during 1 h at 150°C and placed into a vacuum resistant dessicator. Approximately 20 g of polysilazane is heated at 150°C during 10 min to reduce the viscosity and poured on the top of the fibres. The desiccator is closed and the vacuum is operated (500 Pa) and maintained during 1 h. The die is removed from the dessicator. Then the composite is pressed and the die is closed.

The precursor is cross-linked in a muffle furnace under nitrogen atmosphere according to the following temperature schedule: 1 hour at 200°C; 1 h at 250°C; 1 h at 300°C; 30 min at 400°C. After cooling, the composite is removed from the die and is placed in a tubular furnace in flowing nitrogen (100 cm³ min⁻¹) for pyrolysis according to the

following schedule: maximum rate from room temperature (RT) to 400°C, 100°C h⁻¹ from 400 to 1000°C, 1 h at 1000°C, natural cooling. Materials obtained exhibit a high porosity, typically 50%. To obtain high mechanical properties these materials have to be densified by several other cycles of impregnation and pyrolysis.

2.1.2 Powder filled composites

The 'conventional' process has been modified to obtain a quicker densification by reducing the number of impregnation and pyrolysis cycles. A part of the porosity of the fibre preform is filled with submicron silicon nitride powder by soaking the plies of fabric in a slurry made of Si₃N₄ powder (Stark LC10) in iso-propanol (Fig. 2). The plies are then placed in the same die as the one used for 'conventional' composites. The iso-propanol is evaporated in an oven at 150°C during 2 h. The impregnation by the precursor and the pyrolysis are then operated as previously described in Section 2.1.1.

Using a slurry of 40 vol% Si₃N₄ in 60 vol% iso-propanol, the volume ratio of powder/fibres obtained after evaporation of the solvent is 6/10. This means, for a composite with 40 vol% fibres, that 40% of the porosity of the fibre preform is filled with the powder and that only 36% of the volume of the composite remains to be filled with the precursor instead of 60% when using the 'conventional' process.

The initial porosity may even be more reduced by increasing the volume ratio of powder/fibres and this by increasing the volume ratio of Si₃N₄/iso-propanol in the slurry. However, a very high amount of powder damages the fibres when pressing. Therefore, when varying the fibre fraction in the composite, the concentration of the slurry should be adjusted in order that the volume of powder would never become higher than 40% of the porosity of the fibre preform.

2.2 Densification behaviour

The true density of the composites (ρ_{comp}) has been calculated after each of the cycles from the volume fraction (t_{fibre} ; t_{matrix} ; t_{carbon} ; $t_{\text{Si}_3\text{N}_4}$) and the true density (ρ_{fibre} ; ρ_{matrix} ; ρ_{carbon} ; $\rho_{\text{Si}_3\text{N}_4}$) of each of the components using the equation:

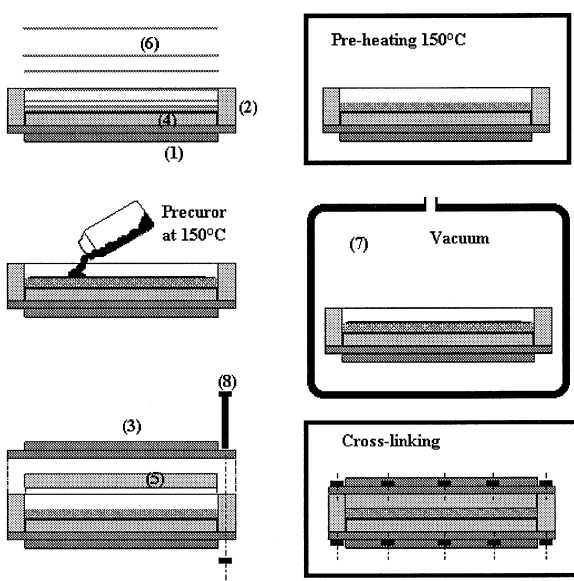


Fig. 1. Process for the first impregnation and pyrolysis: (1) die (bottom); (2) die (main body); (3) die (top); (4) die (1st inside part); (5) die (2nd inside part); (6) plies of fabric; (7) vacuum resistant desiccator; (8) screws.

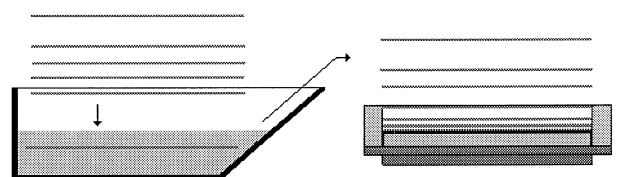


Fig. 2. Impregnation of the fabric with the submicron silicon nitride powder slurry.

$$\rho_{\text{comp}} = t_{\text{fibre}} \cdot \rho_{\text{fibre}} + t_{\text{matrix}} \cdot \rho_{\text{matrix}} + t_{\text{carbon}} \cdot \rho_{\text{carbon}} (+ t_{\text{Si}_3\text{N}_4} \cdot \rho_{\text{Si}_3\text{N}_4}) * \quad (1)$$

(* only for Si_3N_4 filled composites).

The porosity (P) is calculated from the true and apparent density of the composite according to the equation:

$$P = (1 - \rho_{\text{apparent}}/\rho_{\text{comp}}) \cdot 100 \quad (2)$$

This experimental result has been compared with the theoretical porosity (P_n) that the composite is expected to have after n cycles. This theoretical porosity is calculated from the initial porosity P_0 , the ceramic yield Y_c of the precursor and the true density of the matrix (ρ_{matrix}) and precursor (ρ_{prec}):

$$P_n = P_0 \cdot (Y_c \cdot \rho_{\text{prec}}/\rho_{\text{matrix}})^n \quad (3)$$

2.3 Mechanical properties

Room temperature flexural strengths have been measured in three-point bending on a Lloyd 2.5 kN testing machine using a support span $S = 50$ mm and a crosshead speed of 0.5 mm min^{-1} . The average dimensions of the composite test bars were: $l = 55.0$ mm; $b = 8.0$ mm; $w = 3.0$ to 3.8 mm. The load versus displacement curves were recorded and converted into stress versus strain curves. The maximum of the curve gives the flexural strength σ and the slope $d\sigma/d\varepsilon$ when ε is small gives the elastic modulus.

3 Experimental Results

3.1 Densification

3.1.1 Conventional composites

The volume of precursor present in the composite after each impregnation is measured from the weight gain of the composite and shows that the infiltration is almost complete. However, the porosity remaining in the material after pyrolysis is significantly higher than it is expected from the theoretical calculation given by eqn (3) (Fig. 3, curve t1). After eight cycles the porosity is higher than 15% instead of the theoretical 5%. SEM analysis of this composite shows large pores ($> 500 \mu\text{m}$) between each ply of fabric (Fig. 4). Previous investigations have shown that, due to its low viscosity in the temperature range $100\text{--}200^\circ\text{C}$, the polysilazane may flow out of these large pores before being cross-linked.^{4,5} Assuming this amount of released precursor (t_{released}) remains constant during

Porosity (%)

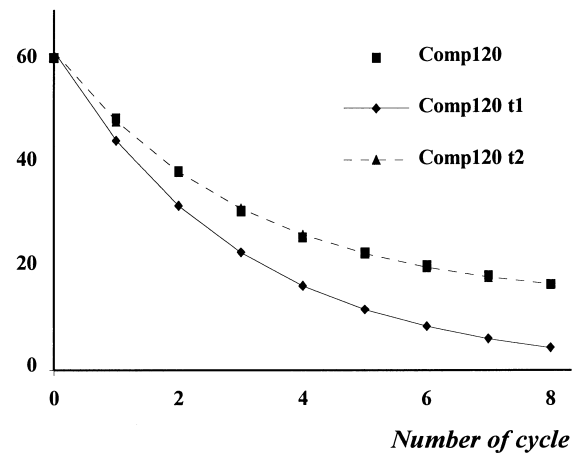


Fig. 3. Porosity as a function of number of cycles for conventional composites (Comp120).

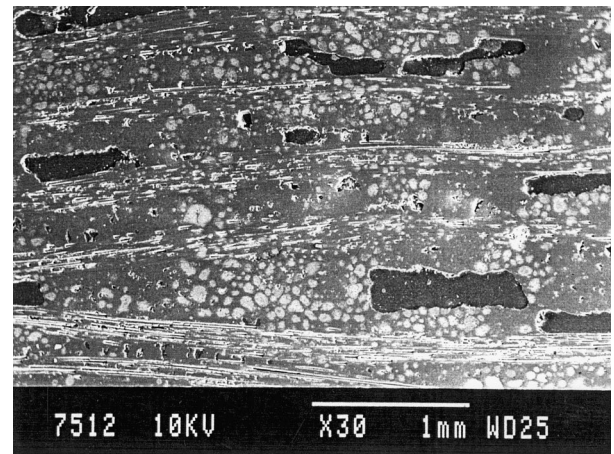


Fig. 4. SEM micrograph of conventional composite Comp120.

the process the theoretical equation of densification becomes:

$$P_n = (P_0 - t_{\text{released}}) \cdot (Y_c/\rho_{\text{matrix}})^n + t_{\text{released}} \quad (4)$$

By adjusting t_{released} to 14% we obtain a theoretical curve corresponding to the experimental values (Fig. 3, curve t2). t_{released} has been calculated from the densification curves of composites having various initial porosity (by increasing the fibre fraction). Figure 5 shows that the amount of released precursor decreases with the initial porosity. Indeed, when the fibre fraction increases, the space between the plies decreases, the pores become smaller and the amount of released precursor decreases.

3.1.2 Powder filled composites

Experimental densification curves obtained with powder filled composites fit exactly with the curves

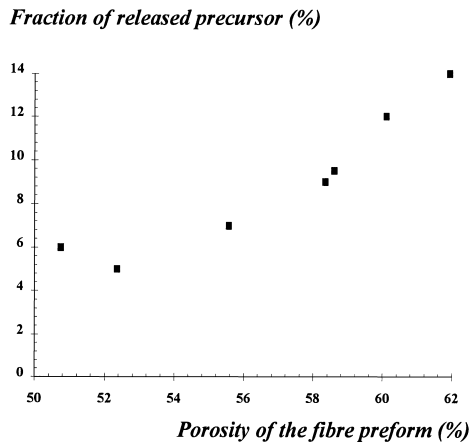


Fig. 5. Fraction of released precursor versus the porosity of the fibre preform.

calculated from eqn (3) (e.g. Fig. 6, curve t1). A porosity lower than 10% is easily achieved after five cycles which is not possible with conventional composites. The SEM analysis shows that the large pores that cause the release of precursor in conventional composites are, with this process, filled with the silicon nitride powder (Fig. 7). The voids remaining between the grains allow retention of the precursor before cross-linking. A deviation to the theoretical curves t1 is observed after four to five cycles when the porosity reaches 16–15%. The porosity remaining between the fibres within the same ply becomes very small and due to its viscosity, the precursor cannot completely fill the pores. The densification slows down.

3.2 Mechanical properties

All the data are summarised in Table 1.

3.2.1 Conventional composites

3.2.1.1 Influence of the fibre fraction. We have seen in Section 3.1.1. that a high fibre fraction

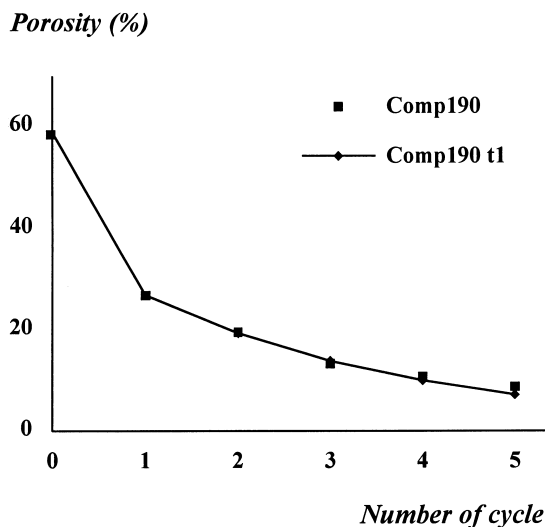


Fig. 6. Porosity as a function of number of cycles for powder filled composites (Comp190).

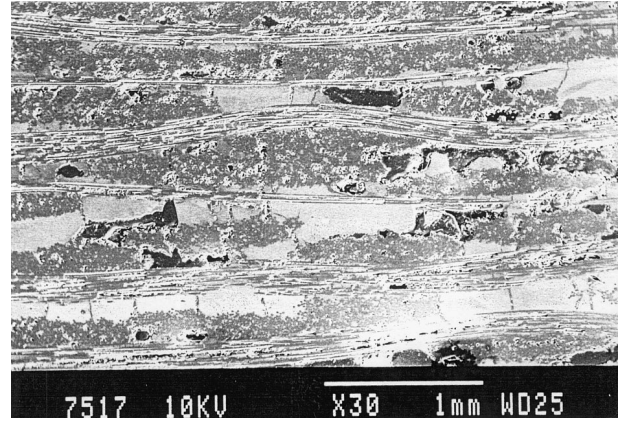


Fig. 7. SEM micrograph of powder filled composite Comp190.

reduces the amount of released precursor and allows a lower final porosity. This should increase the mechanical properties. Experiments show indeed an increase in the Young modulus but on the contrary to what was expected a decrease in flexural strength (Table 2).

The elastic modulus is linked to the volume fraction of each component of the composite according to the following theoretical equation:⁸

$$E_{\text{comp}} = t_{\text{fibres}} \cdot E_{\text{fibres}} + t_{\text{matrix}} \cdot E_{\text{matrix}} \quad (5)$$

Taking into account the porosity P :

$$t_{\text{matrix}} = 1 - t_{\text{fibres}} - P \quad (6)$$

According to this equation, the variation of E_{comp} with t_{fibres} should be linear:

$$E_{\text{comp}} = t_{\text{fibres}}(E_{\text{fibres}} - E_{\text{matrix}}) + (1 - P) \cdot E_{\text{matrix}} \quad (7)$$

Table 1. Mechanical properties of the composites

Ref.	Type	t_{fibre} (%)	Porosity (%)	σ_f (MPa)	ϵ_{max} (%)	E (GPa)
C120	c	35.0	15.7	289.2	0.51	54.1
C170	c	39.2	15.3	272.6	0.46	61.6
C180	pf	36.8	20.5	57.3	0.60	16.4
C181	pf	36.8	16.0	129.1	0.32	43.2
C182	pf	36.8	14.1	124.3	0.21	51.6
C183	pf	36.8	9.5	141.6	0.25	63.7
C190	pf	36.5	8.8	145.8	0.34	48.2
C200	c	49.7	13.5	178.7	0.32	63.2
C210	c	38.9	18.6	216.3	0.58	39.3
C211	c	38.9	17.8	222.9	0.56	39.8
C212	c	38.9	16.4	214.4	0.50	43.0

Type of composite: c = conventional; pf = powder filled.

Table 2. Influence of the fibre fraction on the mechanical properties of conventional composites

Ref.	t_{fibre} (%)	E (GPa)	σ_f (MPa)
Comp120	35.0	54.1	289
↓Δ	+12%	+14%	-6%
Comp170	39.2	61.6	273
↓Δ	+27%	+3%	-34%
Comp200	49.7	63.2	179

The experiment shows, on the contrary, that the increase in the modulus is not proportional to the fibre fraction.

For the same amount of porosity P , the matrix fraction decreases with an increase in the fibre fraction [eqn (6)] so that the ratio of porosity/matrix fraction increases. This suggests that the mechanical properties of the matrix may decrease when the fibre fraction becomes too high. On the other hand, there is no reinforcement of the matrix if the fibre fraction is too low. An optimal fibre fraction exists for approximately 35%.

3.2.1.2 Influence of the porosity. Composites Comp170, Comp210, Comp211, Comp212 and Comp213 have similar fibre fractions. The variations of the flexural strength and elastic modulus as a function of the porosity are shown in Figs 8 and 9. When the porosity decreases, the ratio of porosity/matrix fraction decreases, and the mechanical properties of the matrix network increase. When the porosity decreases from 19 to 15%, the flexural strength increases by 25% and the elastic modulus increases by 30%.

3.2.2 Powder filled composites

3.2.2.1 Comparison with conventional composites. The conventional composite Comp120 and

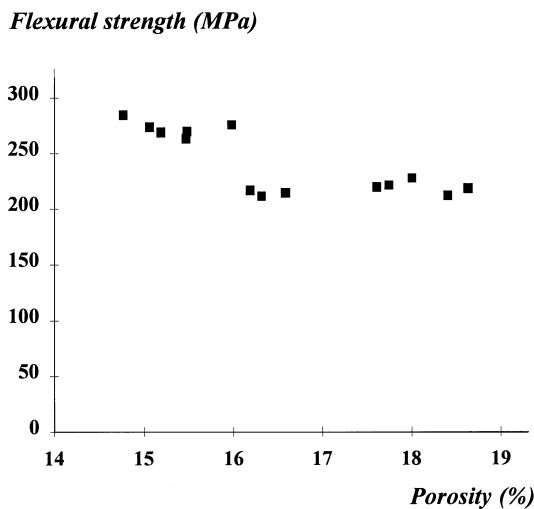


Fig. 8. Flexural strength versus porosity of conventional composites.

Elastic modulus (GPa)

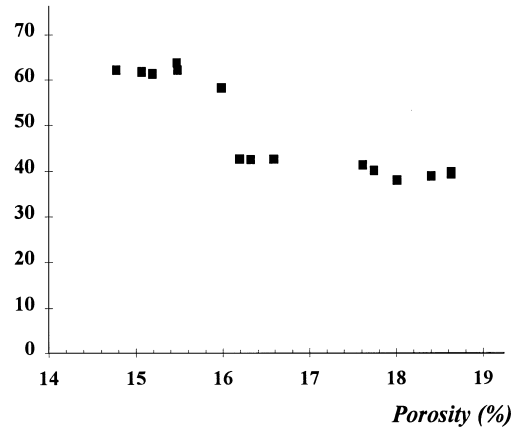


Fig. 9. Elastic modulus versus porosity of conventional composites.

powder filled composite Comp190 have very close fibres fractions (35 and 36.5%, respectively). Despite its lower porosity (8.8% instead of 15.7%), Comp190 exhibits a much lower flexural strength (145 MPa instead of 289 MPa) and a lower modulus (48.2 GPa instead of 54.1 GPa) than Comp120.

In conventional composites, pyrolysed polysilazane represents 45 vol% of the composite and is concentrated around the fibres, whereas the porosity is concentrated between the plies of fabric. The matrix surrounding the fibres is very strong and limits the stress concentration at the fibres surface [Fig. 10(A)].

In powder-filled composites, the matrix is composed of two materials, Si_3N_4 and pyrolysed polysilazane. The Si_3N_4 is essentially concentrated between the plies of fabric, filling the spaces corresponding to the porosity of conventional composites

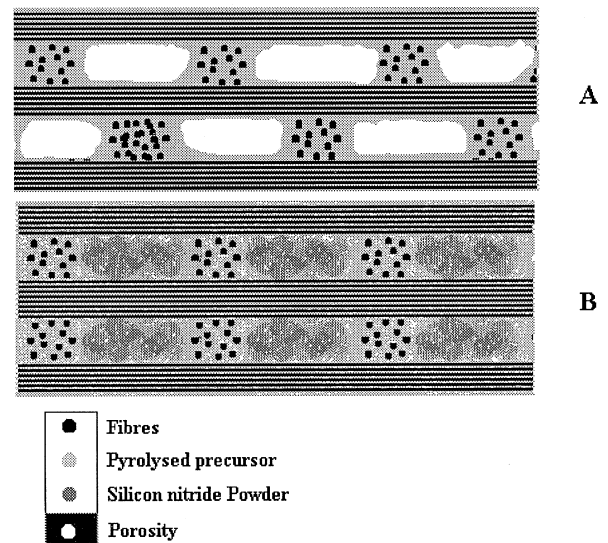


Fig. 10. Structure of the pyrolysed precursor within (A) conventional and (B) powder filled composites.

[Fig. 10(B)]. Instead of being concentrated around the fibres, as for conventional composites, the pyrolysed polysilazane is dispersed throughout the material. The 8% porosity remaining is also dispersed across the composite. According to the low temperature of pyrolysis (1000°C) it is assumed that the bonding between the Si_3N_4 grains and between the Si_3N_4 and the pyrolysed polysilazane is very weak. The mechanical properties of this matrix network are very low and this leads to the low mechanical resistance of the composite.

To improve the mechanical resistance of the matrix, the bonding between powder grains and between powder and pyrolysed polysilazane must be increased. This could be done by increasing the temperature but then there is a risk of fibre damage. An other solution could be to use another type of ceramic powder that may easily react with the polysilazane. A possibility is to use low temperature pyrolysed polysilazane powder.

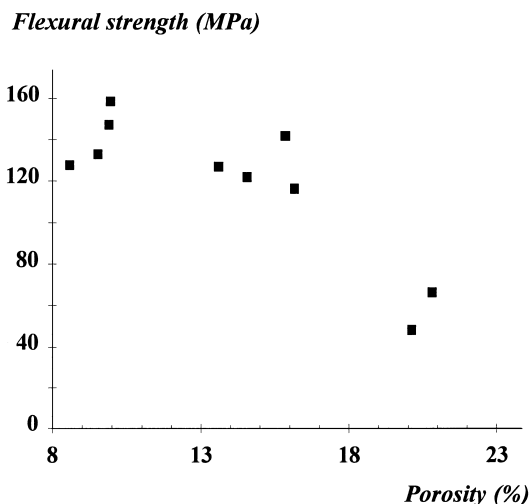


Fig. 11. Flexural strength versus porosity of powder filled composites.

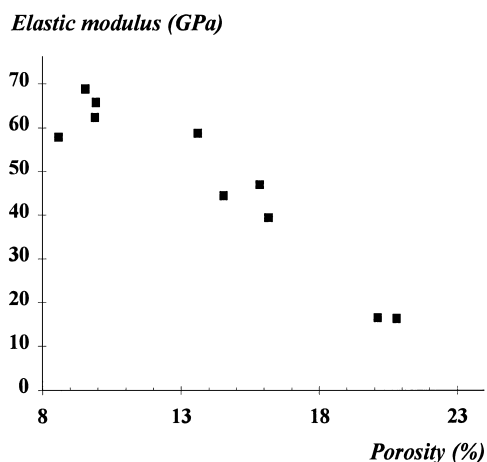


Fig. 12. Elastic modulus versus porosity of powder filled composites.

3.2.2.2 *Influence of the Porosity.* Samples of composite Comp180 have been tested after two cycles (ref. Comp180), three cycles (ref. Comp181), four cycles (ref. Comp182) and five cycles (ref. Comp183). The flexural strength and elastic modulus as a function of the porosity are shown in Figs 11 and 12. As for conventional composites, due to the strengthening of the matrix network the flexural strength and the elastic modulus increases when the porosity decreases, but as previously explained the flexural strengths of the powder-filled composites are much lower than for conventional composites.

4 Summary

The 'conventional' process for manufacturing SiC fibre reinforced silicon carbonitride composites leads to materials with high mechanical properties ($\sigma_f \pm 290$ MPa). Due to a partial release of the precursor impregnating the composite during the pyrolysis the densification of such composites is very slow. Seven to eight impregnations and pyrolysis with the precursor are required to reduce the porosity to approximately 15% and lower porosity cannot be obtained. The mechanical properties strongly depend on this porosity. The flexural strength increases by 25% when the porosity is reduced from 20 to 15%. Therefore the densification must be carried on as far as possible. The fibre fraction also influences dramatically the mechanical properties. A high fibre fraction increases only slightly the elastic modulus but reduces the resistance of the matrix and decreases significantly the flexural strength.

The process using submicron silicon nitride powder to fill the fibre preform prior to the precursor impregnations does not lead to improved materials. The flexural strength of the composites obtained is only 50% of that of the conventional composites ($\sigma_f \pm 160$ MPa). The porosity dispersed across the composite and the low bonding between the elements constituting the matrix leads to a matrix network having low mechanical resistance and explains the low mechanical properties of the composites. A powder reacting at low temperatures with the polysilazane could be used instead of the silicon nitride to improve the resistance of the matrix.

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