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Association of the CVI Process and of the Use of Polysilazane Precursor for the Elaboration of Ceramic Matrix Composites Reinforced by Continuous Fibres

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Abstract

A new process route for ceramic composites, associating CVI of SiC and impregnation and pyrolysis cycles with a polysilazane precursor, has been developed. The interest of this process is, firstly, a shorter time of elaboration than for CVI alone and, secondly higher mechanical properties than those resulting from a conventional use of the precursor. Composites with mechanical properties comparable to those of composites entirely obtained by CVI of SiC have been realised. The flexual strength of these materials is about 400 MPa, whereas that of composites resulting from a conventional use of the same polysilazane does not exceed 200 MPa.

1 Introduction

New materials able to operate under hostile stress–temperature–environment conditions are required for the development of high performance applications (e,.g. aeronautics).

The material used presently (e.g. SiC/C/SiC or C/SiC obtained by CVI) have high mechanical properties (e.g. flexural strength about 400–500 MPa) but their elaboration needs a very long time, and is, therefore, very expensive.[1,2] An alternative way to the CVI process is the use of organometallic precursors leading, after pyrolysis, to ceramic products. However, to date, the mechanical properties of the material obtained by this method are not able to compete with those of composites resulting from the CVI route (e.g. flexural strength lower than 200 MPa.[3–5]

The 'conventional' use of the precursor consists of a sequence of successive impregnation and pyrolysis cycles of a fabric preform with the precursor. The matrix obtained is composed of numerous ceramic blocks corresponding to the successive cycles (Fig. 1(a)). Such a structure is not as strong as the continuous one resulting from the CVI route (Fig. 1(b)). Indeed, the interfaces between the different blocks create some weak points. Moreover, when these interfaces are perpendicular to the loading direction, they lead to stress concentrations on the fibre surfaces what may cause the fracture of these fibres (Fig. 1(a)). This can explain the low mechanical properties of such composites. On the other hand, the deposition rate by CVI is very low. Therefore, the elaboration of dense composites by this process needs a very long time.

The basic idea of this study is, firstly to elaborate a high porosity composite preform by CVI of SiC on bidirectional SiC Nincalon fabrics and, secondly, to fill the porosity by successive impregnation and pyrolysis cycles with the polysilazane (Fig. 1(c)).

2 Experimental

2.1 Characteristics of Pyrofine PV Polysilazane

The precursor used is a commercial polysilazane produced by Elf Atochem: Pyrofine PV.[6] At room temperature, this product is a viscous liquid (density = 1). Its viscosity decreases with the increase of temperature up to 200°C (Table 1).

Upon heating to 300°C under introgen, the precursor becomes cross linked. the product obtained is solid unmeltable and insoluble.

Pyrolysis under a nitrogen atmosphere at a temperature between 900°C and 1400°C yields an amorphous ceramic. At 1000°C, the ceramic yield varies form 60 to 65 wt%, depending on the heating rate used during the crosslinking.[7] The typical elemental composition of the ceramic obtained is

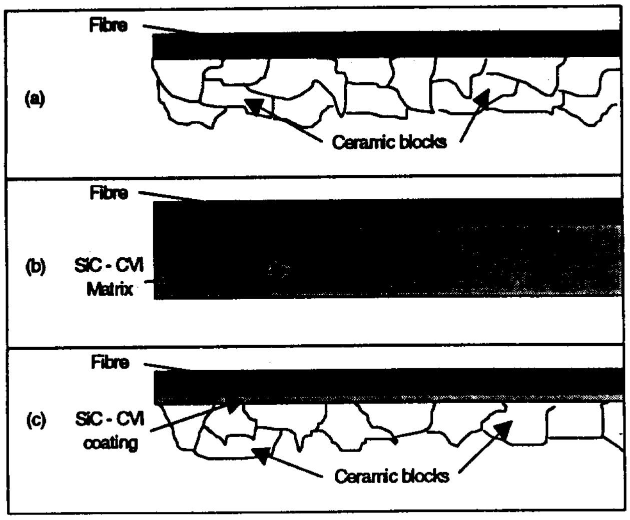

Fig. 1. Structure of the ceramics matrix obtained from (a) an organometallic precursor (b), in the case of CVI process and (c) in the present process.

given Table 2 (oxygen originates from the precursor). The density measured by He psycnometry is 2·13 g/cm^3. Thus, the volumetric yield of the transformation is about 30%.

2.2 Characteristics of the composite preforms

Starting materials are 3·0 to 3·2 mm thick plates. They are composed of eight woven layers of Nicalon NL 202 S8 fabric (from Nippon Carbon).

The fibres volume ratio is about 40 vol.%. A 0·5–1·0 μm thick graphite carbon coating of the fabric is used to limit fibres–matrix bonding and thus, to lead to the unbrittle behaviour of the materials.[8]

A 1·0–2·0 μm thick SiC coating is then realised by CVI.

The porosity determined by Archimedes' method is 36·8 ± 1% and is in agreement with the 38·6 ± 1·3% corresponding to the theoretical calculated value.

2.3 Densification process

To reduce the porosity and then to increase the mechanical properties, successive impregnation and pyrolysis cycles are realised with the polysilazane.

Table 1. Variation of the viscosity of Pyrofine PV polysilazane versus temperature

Temperature,	°C	50	100	150
Viscosity,	mPa.s	1000	100	20

Table 2. Composition of the ceramic obtained from Pyrofine PV polysilazane after pyrolysis at 1000°C

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

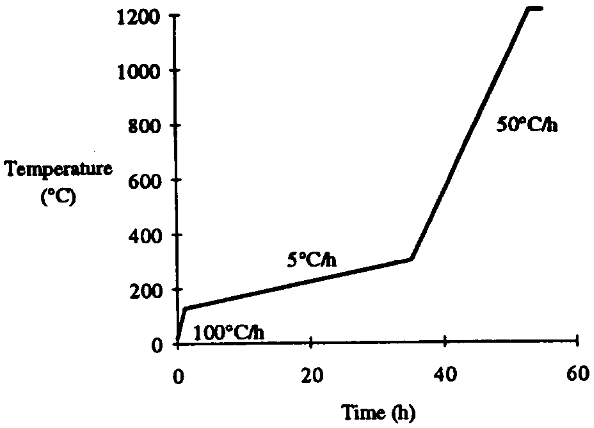

Fig. 2. Pyrolysis temperature schedule of Pyrofine PV polysilazane.

The preforms are charged into a reactor and degassed under 500 Pa at 150°C for 2 h. Thereafter, the precursor, preheated at 150°C to reduce its viscosity, is injected into the preform by means of a pressure gradient between the outside (nitrogen atmospheric pressure) and the inside of the reactor. After injection, preforms are soaked in the precursor at 150°C for 2 h under a nitrogen atmosphere before being removed and placed in the pyrolysis furnace.

Pyrolysis is operated under nitrogen according to the following temperature schedule: 100°C/h up to 130°C; 5°C/h from 130°C up to 300°C; 50°C/h from 300°C up to 1200°C + 4 h hold (Fig. 2).

A separate study has shown that pyrolysis up to 1400°C leads to the highest mechanical properties of the ceramic matrix.[7] However, the thermal resistance of Nicalon fibers limits the temperature of pyrolysis to 1200°C.

2.4 Measure of the physical and mechanical properties

The pore volumes were determined after each impregnation—pyrolysis cycle by Archimedes' method (open porosity) and from the theoretical calculation (total porosity) based on the volume ratio of the components and their absolute density.

The pore size distribution was determined by mercury porosimetry on the preform and after 1, 2 and 5 cycles.

Room-temperature flexural strengths were measured in three-point bending on a Schenck RM-T 25 kN using a support span of 50 mm and a crosshead speed of 0·5 mm/min. The average dimensions of the composite test bars are 65 × 10 × 3 mm^3.

Youngs modulus was determined from the load displacement curves.

Due to the unbrittle behaviour of the materials. The characterisation of the composite toughness requires the calculation of the resistance to crack

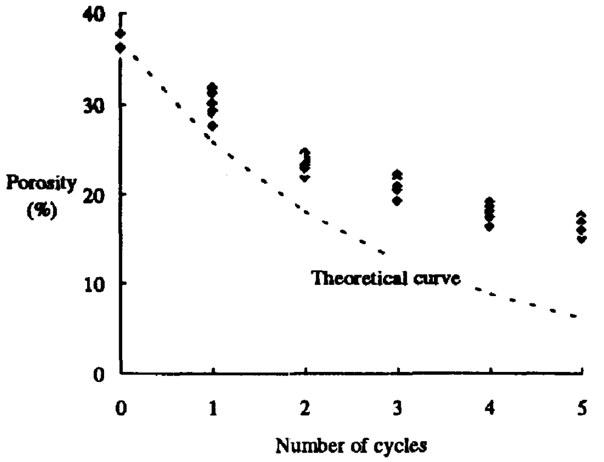

Fig. 3. Variation of the porosity of the composites according to the number of impregnation pyrolysis cycles.

propagation curves (*R*-curves). These curves show the stress intensity factor *K* versus the ratio of the crack length increase, d*a*, to initial ligament thickness of the test bar *w*–*a*. The measures were made by the single-edge notched-beam techinque (SENB) with *a*/*w* = 0·5 (*a*, initial crack length; *w*, thickness of the test bar). According to Bouquet *et al.* and R'mili,[9,10] calculations of d*a* and *K* have been based on the assumption of a linear–elastic behaviour.

3 Results

3.1 Variation of the porosity with the number of cycles

Archimedes' method (open porosity) and the theoretical calculation (total porosity) lead to similar results: the porosity is essentially open.

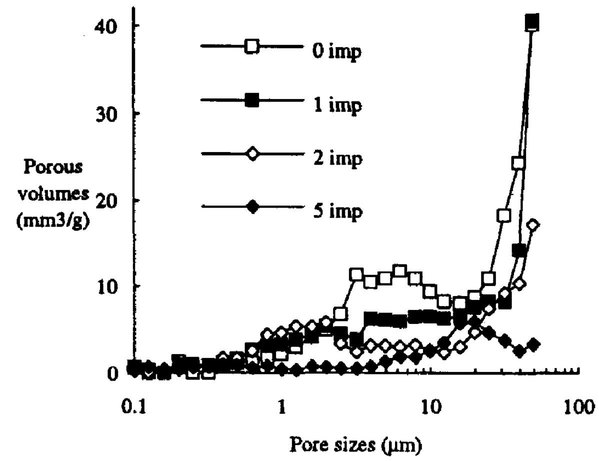

Fig. 4. Pore sizes distribution of (□) the preform and composites after (■) 1, (◇) 2 and (◆) 5 cycles.

The experimental porosity–number of cycles curve deviates for the theoretical one corresponding to a complete impregnation of the samples (Fig. 3). After five cycles, the porosity tends to an asymptotic value between 10 and 15%. The porosity being essentially open, this may be due to fine porosity which, due to the viscosity of the precursor, cannot be filled during the impregnation. However, weighing the composites after the precursor injection indicates that 96–97% of the free volume is filled.

On the other hand, after each pyrolysis, a residue of pyrolysed precursor is present at the bottom of the reactor. It is therefore concluded that the deviation between the experimental and theoretical porosity evolution curves is mainly due to the release of precursor during the early stage of pyrolysis, while its viscosity is still low (temperature range 150–200°C).

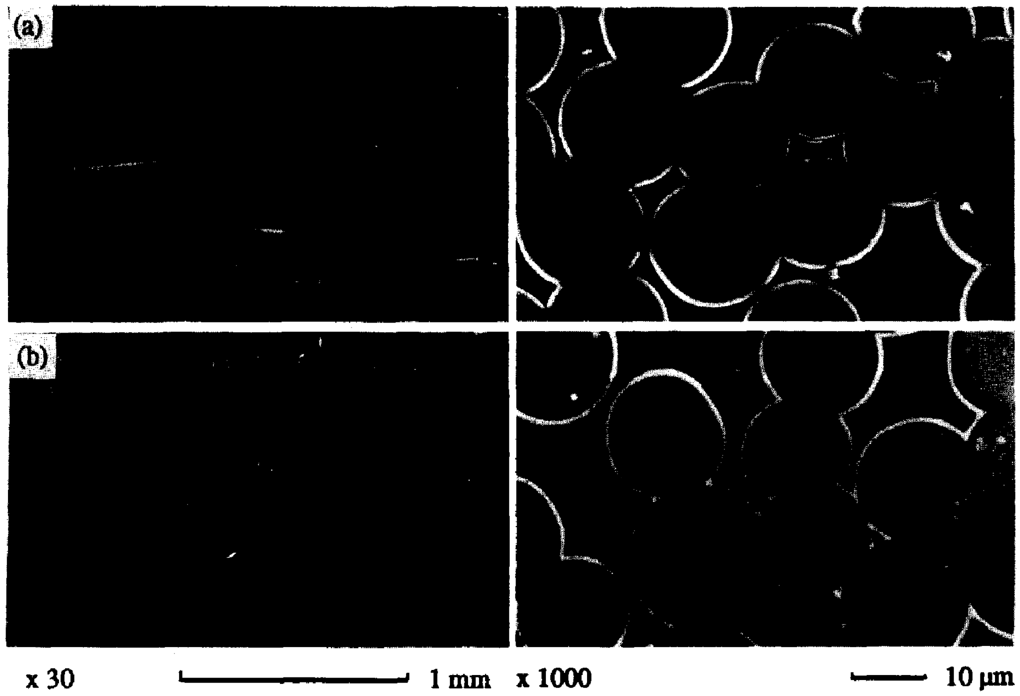

Fig. 5. SEM observation of the cross-sections of the composites (a) before the impregnation–pyrolysis cycles with the polysilazane and (b) after 5 cycles.

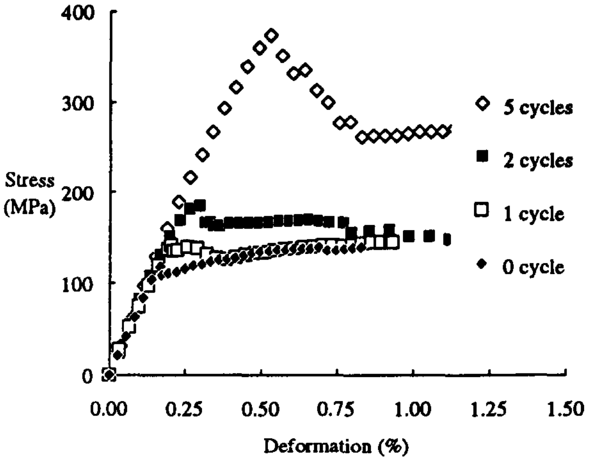

Fig. 6. Composite stress–deformation curves obtained in three-point bending.

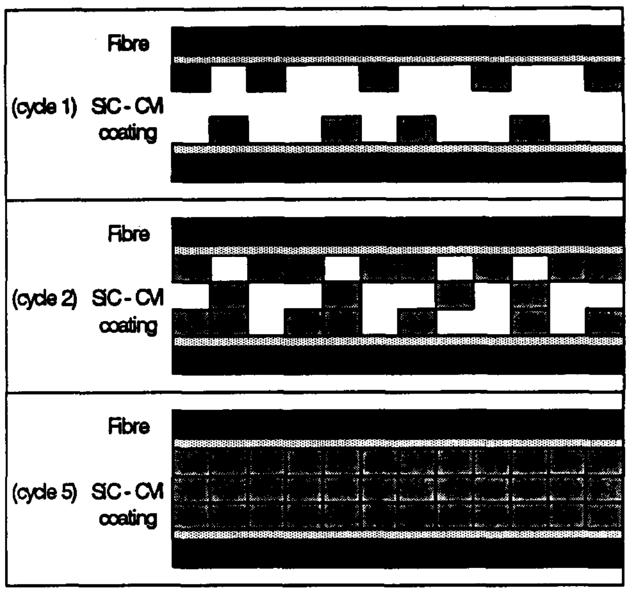

Fig. 8. Processing of the ceramic matrix during the successive impregnation and pyrolysis cycles with the polysilazane.

The pore size distribution was determined on the preform and after 1, 2 and 5 cycles. Two classes of pores are observed on the pore volume distribution graph (Fig. 4): firstly 1–10 μm radius pores corresponding to the space which separates the fibres within a same cloth; this porosity decreases readily according to the number of cycles; and secondly, pores with a radius larger than 50 μm, corresponding to the voids between two woven cloths. This porosity starts decreasing only after the second cycle. A SEM observation shows the good filling of the interfibres voids, whereas the space between cloths is only partially filled (Fig. 5(a) and (b)). This seems to confirm that the precursor could flow out of the largest process before the crosslinking.

3.2 Variation of the mechanical properties with the number of cycles

The stress–deformation curves obtained (Fig. 6) show the unbrittle behaviour of the materials. This is the result of the weak fibre–matrix interface. Samples of preform and of composites after one and two cycles fail in a shear mode by delamination between the plies. Their flexural strengths are similar, about 150 to 180 MPa, corresponding to a delamination strength of about 10 MPa.

On the other hand, the failure of the composites obtained after five cycles is perpendicular to the fabrics. The flexural strength is higher, 400 MPa, and a large amount of fibre pullout is observed on the fracture surfaces. A similar evolution of the failure mode according to the number of cycles is observed by Boisvert & Diefendorf.[3]

The Young's modulus versus porosity curves show a three-stage variation (Fig. 7).

The ceramic residues of the first cycle are too dispersed to build a continuous network (Fig. 8, 1 cycle). Their contribution to the composite elastic modulus is low. No siginficant increase is ascer-

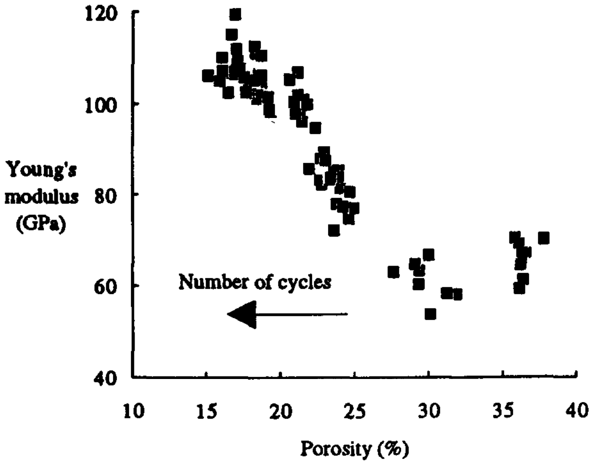

Fig. 7. Variation of the Young's modulus versus the porosity of the composites.

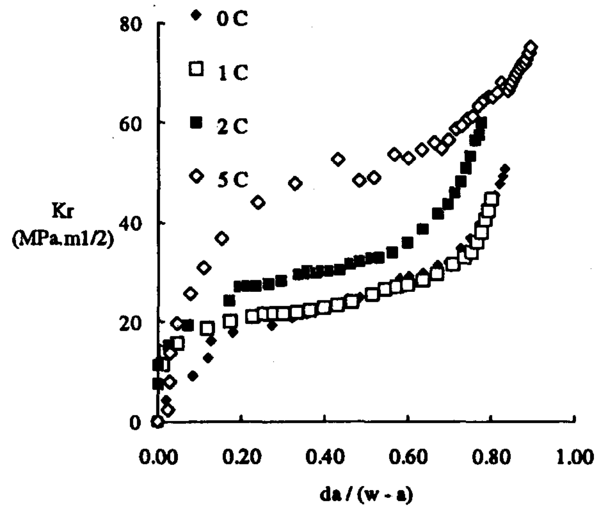

Fig. 9. R-Curves obtained on the assumption of a linear–elastic behaviour.

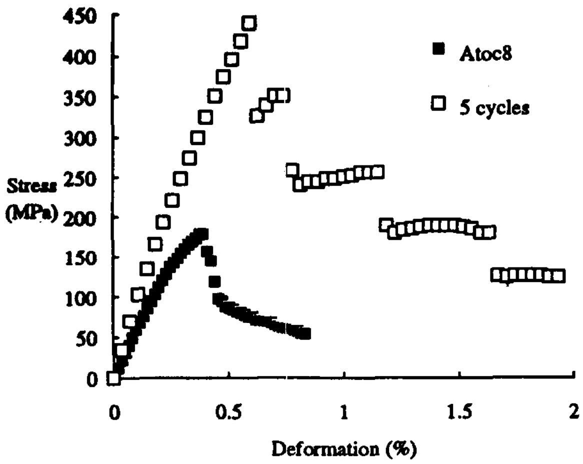

Fig. 10. Stress–deformation curves in three-point bending of composites elaborated from the new process (CVI + 5) and from the conventional one (Atoc8).

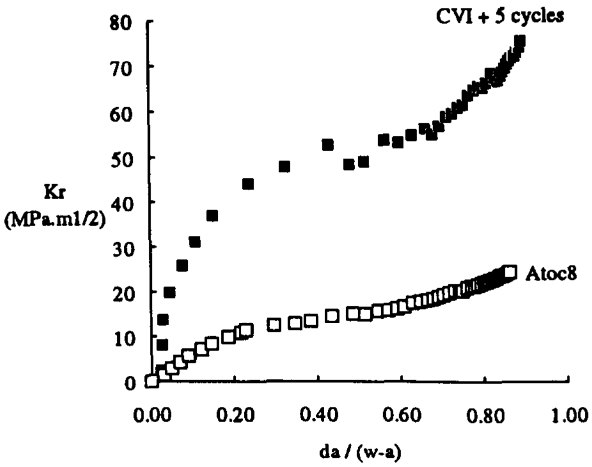

Fig. 11. *R* curves of composites elaborated from the new process (CVI+5) and from the conventional one (Atoc8).

tained. Then, the decrease in porosity from 30 to 22% leads to a large increase in the modulus. The ceramic blocks corresponding to the second and third cycles create progressively a ceramic 'framework' (Fig. 8, 2 cycles).

Thereafter, this framework is filled and strengthed (Fig. 8, 5 cycles). This corresponds to the more gradual increase in modulus when the porosity decreases below 20%, that is to say, during the fourth and fifth cycles.

As expected, the *R*-curves show that *K* increases with the crack length (Fig. 9). Indeed, in addition to the generation of new surfaces, several energy dissipative mechanisms occur during crack propagation, leading to the increase in the crack propagation resistance. The variation of these curves as a function of the number of cycles is similar to that of the flexural strength.

The curves obtained with the preforms and after one or two cycles are almost superimposed, whereas those obtained after five cycles are significantly higher. This can also be explained by the evolution of the failure mode. After the first cycles the cracks are propagated only through the matrix, the crack propagation resistance is low. On the opposite after five cycles, the crack propagation is perpendicular to the fabrics. In this case, the weak fibre matrix interface allows several energy dissipative mechanisms (e.g. fibre pull-out, interface debonding, etc.), increasing the resistance to the crack propagation.

3.3 Comparison with a conventional use of the same percursor

Another type of composite has been realised from a conventional use of the same percursor when the fibres are coated with pyrolytic carbon and placed in an injection mould. The impregnation process is similar to the one described above.

The materials have been tested in three-point bending. The values of the mechanical properties are listed in Table 3. The stress–deformation curves and the *R*-curves obtained in this case (Figs 10 and 11) are siginficantly lower than those obtained with the process CVI + precursor. The flexural strengths of the composites are lower than 200 MPa compared to 400 MPa for the first process and the elasticity modulus does not exceed 70 GPa compared to 105 GPa. Nevertheless, these results are comparable to those obtained with some other precursors used in a similar process.[3–5]

Table 3. Mechanical properties o the composites

Process route	*Ref. comp.*	*Cycle number*	*Fibre Ratio (vol.%)*	*Carbone coating (μm)*	*Porosity (%)*	*Flexural strength (sf) (MPa)*	*Young's modulus (E) (GPa)*
Conventional	Atoc6	8	49	0·50	10·4 ± 0·6	166 ± 27	81 ± 4
Conventional	Atoc7	8	49	0·25	13·6 ± 0·9	159 ± 13	62 ± 6
Conventional	Atoc7b	9	49	0·25	11·8 ± 1·1	168 ± 21	85 ± 5
Conventional	Atoc8	7	41	0·20	17·0 ± 0·7	179 ± 22	55 ± 3
New	CVI+0	0	38·5	0·5 ± 1·0	36·8 ± 1·0	156 ± 20	65 ± 10
New	CVI+1	1	38·5	0·5 ± 1·0	29·8 ± 1·1	135 ± 11	69 ± 4
New	CVI+2	2	38·5	0·5 ± 1·0	23·5 ± 1·5	185 ± 23	95 ± 6
New	CVI+5	5	38·5	0·5 ± 1·0	16·4 ± 1·3	376 ± 62	103 ± 11

4 Conclusion

This new process route leads to high mechanical property composites. Only five impregnation–pyrolysis cycles with Pyrofine PV polysilizane on the SiC/C/SiC preforms are required to increase the flexural strength form 149 to 380 MPa and the Young's modulus from 65 to 105 GPa. The toughness follows the same evolution. These results are comparable to those of composites entirely obtained by CVI and SiC and siginficantly higher than those obtained by a conventional use of the same precursor (flexural strength lower than 200 MPa). However this process is not as fast as expected. Indeed, after each cycle, the porosity decreases less than calculated from the volumetric yield of the percursor during the pyrolysis. The porosity is 15% after five cycles instead of the 7% expected. This is due to the release of the precursor from the preform during the early stage of the pyrolysis.

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