

# Mechanical properties of ceramic matrix composites with siloxane matrix and liquid phase coated carbon fiber reinforcement

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Available online 13 September 2004

## Abstract

In order to evaluate the benefits of continuous liquid phase coating (CLPC) for carbon fibers, coated fibers as well as uncoated fibers were applied in the preparation of unidirectionally reinforced ceramic matrix composites (CMCs) with polysiloxane based matrix. Fibers coated with precursor based ceramic or carbon coatings were transferred into prepreps by continuous fiber impregnation with liquid polysiloxane and filament winding. The wet prepreps were cut to shape, laminated and then pressed and cured in the mold at 150 °C for 1 h. The cured polymeric matrix composites were calcined and densified by subsequent precursor infiltration/calcination cycles. The flexural strength of the CMCs was measured by 4-point bending tests, the microstructure was determined by optical and scanning electron microscopy. The application of CLPC coated fibers led to a significant improvement in composite strength and young's modulus compared to identical reference samples with uncoated carbon fibers.

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*Keywords:* Composites; Precursor; Liquid phase coating; Carbon fibers

## 1. Introduction

Carbon fibers are very frequently used as reinforcement in composite materials because of their high mechanical strength and low price. While carbon fiber reinforcement in polymeric matrix composites is widespread, the use of carbon fibers in ceramic matrix composites is still limited due to the fact that the fibers may suffer from damage by hot corrosion, oxidation and mechanical stress during manufacturing and application. The deposition of protective coatings can help to overcome these problems. The state of the art coating technology, chemical vapor deposition (CVD) is rather costly by low deposition rates and high investment costs,<sup>1</sup> so that the application of CVD coated fibers is mostly limited to high-end aerospace applications. Another important property in composites which can be adjusted by deposition of coatings is the fiber matrix adhesion which has to be properly adjusted in order to be able to use the fiber strength at full capacity.<sup>2,3</sup> Continuous liquid phase coating is a technically feasible method to provide ceramic or carbon coatings

for fiber strands at a reasonable price.<sup>4–6</sup> In a pilot plant CLPC facility, commercially available 12K rovings of high tenacity carbon fibers are thermally desized under nitrogen, and then continuously coated with a diluted precursor solution. The polymeric coating is subsequently dried, cured, pyrolyzed and calcined in inert atmosphere to obtain a dense and homogenous coating on each monofilament of the fiber strand. The coated rovings do not stick together and are suitable for further textile processing. Coatings can be produced from organosilicon precursors yielding SiCO, SiCN, SiBCN or SiC and from phenolic resins and coal tar pitches yielding amorphous or graphitic coatings. The coating thickness ranges from 100–500 nm. The tensile strength of the fibers was optimized by factorial design experimental planning.<sup>7</sup>

In this study we tried to investigate the effect of the CLPC fiber coating on the composite strength and fracture behaviour. For this purpose we chose a fiber-matrix system in which no reactive interaction between matrix and fiber during manufacturing is to be expected and which is easy to process. The polysiloxanes do significantly shrink during pyrolysis and calcination imposing residual stress on the fiber matrix interface. The coatings should help to partially decouple fiber and matrix and thus decrease the stress on the fiber. Thus we

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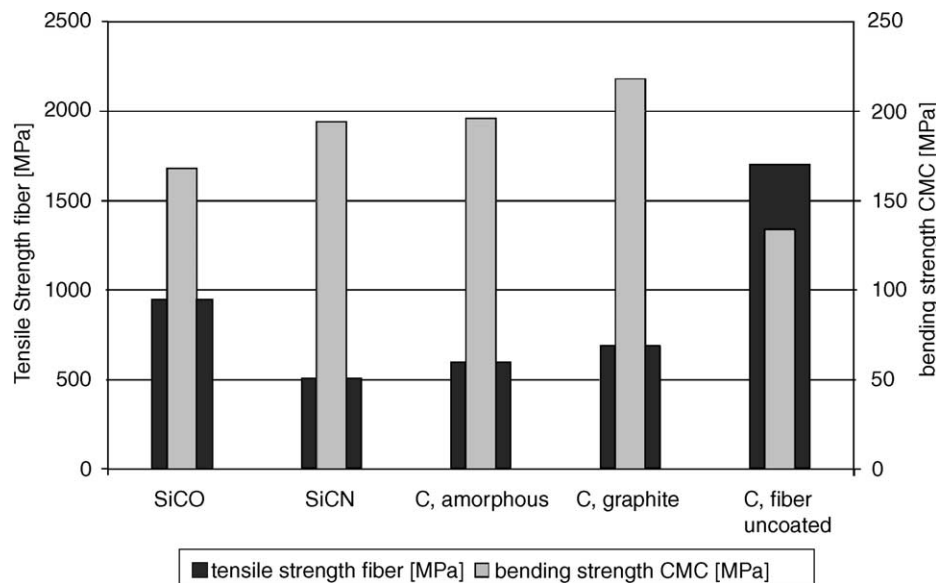


Fig. 1. Bending strength of composites vs. tensile strength of reinforcement fibers, three densification cycles, matrix polymer Wacker SilresH62C, calcination temperature 750 °C.

expected higher composite strength with coated fibers. In order to quantify the effect of different fiber coatings we did not suppress the matrix shrinkage by introduction of passive ceramic fillers.<sup>8</sup> In a study recently published<sup>9</sup> we had evaluated different types of fibers by production of laboratory samples derived from dry filament winding and precursor infiltration in an open mold. The results (Fig. 1) showed, that coatings do have an effect on composite strength. The types of coated fibers used in the preliminary investigations are listed in Table 1. We then tried to evaluate the potential of the CMCs by application of pilot plant manufacturing equipment which should lead us to better and more reproducible results.

## 2. Experimental

CLPC-fiber coatings were produced from commercial Tenax HTA 5411 high tenacity 12K carbon fiber strands. The fibers were continuously desized under flowing nitrogen at 700 °C. The desized fibers then pass a reactor where the fibers are looped around several guiding rollers in a vessel filled with a diluted precursor solution (Table 1). The fiber strand is immediately filled with liquid due to capillary forces, a spreading of the fiber is not required for homogenous deposition. The coated strand then enters a set of four furnaces. In the first furnace the solvent is evaporated at 375–475 °C, in the

second furnace the polymer is crosslinked at 600–650 °C. After the second furnace the fiber strand which is stuck together by the crosslinked polymer is wound around a draw panel of 100 mm diameter which runs at 8–12 m/h. This draw panel transports the fiber forward and individualizes the monofilaments by breaking the polymer bridges between the filaments. The pyrolysis and ceramization of the fiber is carried out in two furnaces at 750 °C and 800–1200 °C. After the fourth furnace the ceramic coated roving is wound around another draw panel of 100 mm diameter which runs at the same speed as the first one. Finally the fiber is wound on paper rolls. All processes are synchronized, so that the commercial fiber is converted into a coated fiber in a continuous process. The tensile strength of the fibers was determined in a multifilament test according to DIN 65382.<sup>10</sup>

For material screening composites were manufactured from coated Tenax HTA 5411 high tenacity carbon fibers and polysiloxane. Samples were prepared by winding of dry filaments with subsequent vacuum infiltration with Wacker Silres H62C in a small mold for test beams (100 mm × 8 mm × 3 mm). Samples were stabilized in air at 200 °C/2 h and calcined at 750 °C for 6 h. The mechanical properties were determined after three densification cycles by 4-point bending tests according to DIN V ENV 658.<sup>11</sup> The test results (Fig. 1) show that fiber coatings have a strong influence on composite performance. Best results were obtained with coat-

Table 1

Coating precursors, dilution, solvent, calcination conditions and coating material yielded in continuous liquid phase coating

Precursor	Dilution (mass%)	Solvent	Calcination	Coating material
Siloxane Wacker Silres H62C	5	Acetone	750	SiCO
Silazane ABSE University Bayreuth [9]	3	Methylethylketone	1000	SiCN
Phenolic resin Bakelite 9691 FW	2.5	Ethanol/acetone	1000	C, amorphous
Carbores F Rütgers Chemicals	5 (toluene extract)	Toluene	1000	C, graphitic

ings of graphitic carbon derived from coal tar pitch extracts. Silicon carbonitride and amorphous carbon also lead to a significant increase in strength. Even a coating with the matrix material improves the composite performance. The reference sample with reinforcement by pyrolytically desized carbon fibers (700 °C, nitrogen atmosphere) has only a poor performance although the fibers have the highest tensile strength in a multifilament tensile test according to DIN 65382.

As this method was not suitable for production of larger scale samples we scaled the procedure up. The carbon fibers (both coated and uncoated) were impregnated with the liquid matrix precursor by passing through a 5 L tank where the precursor (Wacker Silres H62C) was pressed into the space between the filaments by alternating guiding rollers of 50 mm diameter. Wet fiber prepregs were produced by winding the impregnated roving on an octagonal drum with an edge length of 250 mm and a width of 400 mm. The fibers were aligned with a spacing of less than 0.5 mm to avoid any crossover. After two layers were complete, the prepregs were cut off the drum for further processing. The prepregs were then cut to shape for pressing (160 mm × 280 mm for the warm press). Warm pressing was carried out with a pressure of 18 MPa at a processing temperature of 150–200 °C in a Schuler Hydrap hydraulic press. After 30–120 min the cured samples were taken from the mold and calcined at 750 °C for 6 h in inert atmosphere. In order to improve the mechanical properties of the samples the as fired samples were cut to smaller pieces dried and reinfiltred with a polysiloxane of low viscosity (Wacker Silres MSE100). The samples were again cured at 200 °C and calcined at 750 °C. Up to three densification cycles were carried out.

Specimens suitable for mechanical characterization by a 4-point bending test according to DIN V ENV 658 were cut from the composites, sample dimensions were usually 120 mm × 10 mm × 3.4 mm. For each experiment 3–6 samples were tested. All samples were tested as cut without surface finishing. The fiber and porosity distribution of cross cut

and polished samples was determined by optical microscopy, the fractured surfaces were investigated by SEM.

### 3. Results

#### 3.1. Influence of densification

The influence of densification was determined by re-infiltration of composites with Wacker Silres H62C based matrix and amorphous carbon coated reinforcement fibers. The results obtained (Fig. 2) show that the mechanical strength reaches an optimum at two densification cycles. The Young's Modulus increases with subsequent densification. The microstructure and fracture surfaces (Fig. 3) show that the fiber-matrix interface is very weak in case of poorly densified matrix, thus the composites fail by delamination, highly densified composites show brittle failure. At the optimum the matrix is not fully densified yet slight delaminations can be observed and the fracture surfaces show some pull-out behaviour.

#### 3.2. Influence of calcination temperature

In order to determine the influence of the calcination temperature, identical samples were prepared and calcined at 750 and 900 °C. Two densification cycles were carried out. The mechanical properties of the samples were determined by 4-point bending tests. The reinforcement fibers were SiCN-coated (Table 1) and showed low tensile strength in a multifilament test (<500 MPa). The matrix polymer was Wacker Silres H62 C for the initial manufacturing step and Wacker Silres MSE 100 for the densification. The samples were manufactured from wet prepregs which were laminated and warm pressed. The results show that the composites have better mechanical properties at lower calcination temperatures (Table 2).

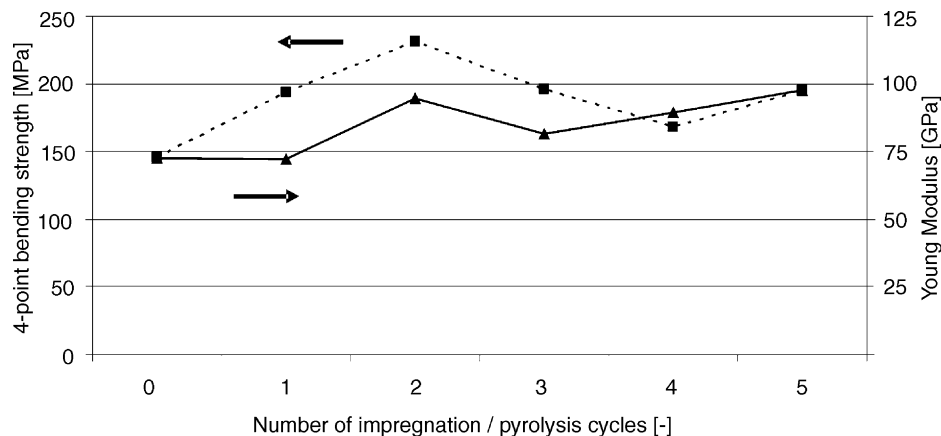


Fig. 2. Mechanical properties of composites depending on the number of densification cycles, fiber Tenax HTA5411, coated with 2.5 mass% Phenolic resin Bakelite 9691 FW, calcined at 1000 °C, Matrix Wacker Silres H62C, calcination temperature 750 °C.

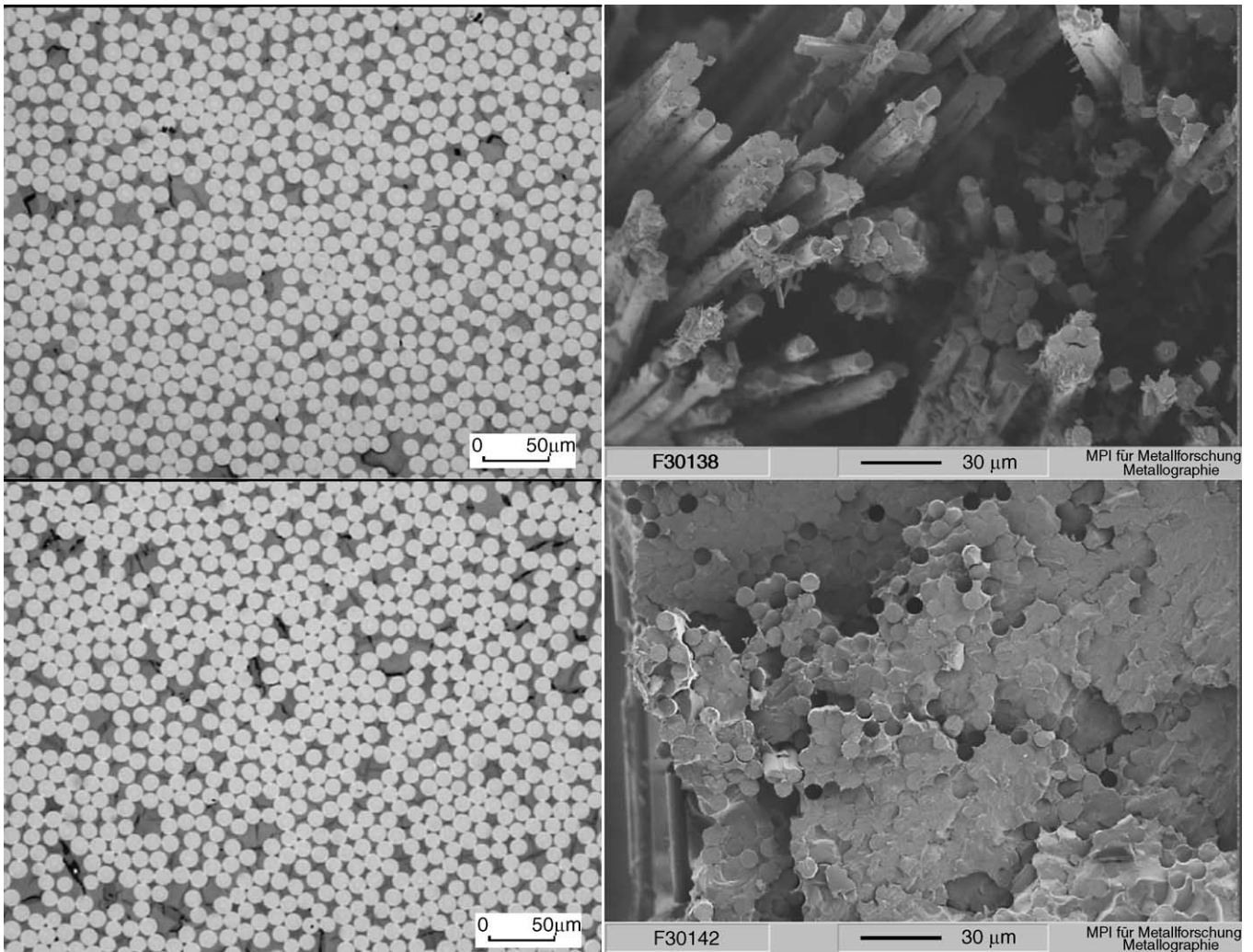


Fig. 3. Cross sections (left) and fracture surfaces (right) of carbon fiber reinforced siloxanes depending on densification, fiber Tenax HTA5411, coated with 2.5 mass% Phenolic resin Bakelite 9691 FW, calcined at 1000 °C, Matrix Polymer Wacker Silres H62C, calcination temperature 750 °C. top: after one densification cycle (left optical micrograph, right SEM micrograph), bottom: after two densification cycles (left: optical micrograph, right: SEM micrograph).

Table 2

Mechanical properties of composites, reinforcement Tenax HTA 5411 coated with SiCN, matrix polymer Wacker SilresH62C, densification with Silres MSE 100, calcination temperatures 750 and 900 °C, 0–2 densification cycles

Number of densification cycles	750 °C			900 °C		
	Bending strength ( $\sigma$ ) (MPa)	Young's modulus (GPa)	Strain to failure ( $\epsilon$ ) (%)	Bending strength ( $\sigma$ ) (MPa)	Young's modulus (GPa)	Strain to failure ( $\epsilon$ ) (%)
0	248	143	0.36	142	64	0.28
1	413	168	0.23	252	109	0.21
2	365	162	0.22	259	122	0.20

#### 4. Summary

Carbon fiber reinforced composites derived from liquid phase coated carbon fibers and polysiloxane based silicon oxycarbide matrix were produced. The influence of fiber coatings, number of densification cycles and of calcination temperature was investigated. Best results were obtained with carbon and silicon carbonitride coatings leading to a sig-

nificant increase in composite strength. The coatings lead to a decoupling of fiber and matrix during processing and improved fiber-matrix interface properties. In order to be able to evaluate the fiber-interface properties it is important to compare the thermal expansion coefficients of all constituents and the elastic mismatch between fiber and matrix. Polysiloxane based silicon oxycarbides have a thermal expansion coefficient (CTE) between  $3.1 \times 10^{-6} \text{ K}^{-1}$  [12] and

$3.5 \times 10^{-6} \text{ K}^{-1}$ ,<sup>13</sup> silicon carbonitride based on ABSE<sup>14</sup> precursor has a CTE of  $8.05 \times 10^{-6} \text{ K}^{-1}$  at 750 °C according to own measurements, HT carbon fibers used have a CTE or  $-0.1 \times 10^{-6} \text{ K}^{-1}$  in axial direction and a CTE of approx.  $8 \times 10^{-6} \text{ K}^{-1}$  in radial direction (manufacturer data). According to the model of He and Hutchison<sup>15</sup> the fiber matrix interface should be under tensile stress and the elastic mismatch between fiber and matrix should be as high as possible. The Young's modulus of H62C siloxane pyrolyzed at 750 °C is 35 GPa (56 GPa pyrolyzed at 900 °C), the Young's modulus of bulk ABSE polysilazane derived SiCN pyrolyzed at 1000 °C is 114 MPa according to own microhardness measurements, the Young's modulus of the fibers is 238 GPa in axial direction. Though the properties of 100 nm thin coating layers shrunk on the fiber during liquid phase coating will differ from the properties of bulk material we may conclude that: After cooling from 750 °C to room temperature the fiber surface is under compressive stress and the coating surface is under tensile stress. This is an improvement compared to uncoated fibers in contact with siloxane matrix. The elastic mismatch of fiber and coating is +0.35 the elastic mismatch of coating and matrix is +0.53 for matrix calcined at 750 °C and +0.34 for matrix calcined at 900 °C. This can be one reason for the lower mechanical strength of the composites calcined at higher temperatures. Densification of the matrix strongly influences the mechanical properties. The bending strength rises to a maximum at 1–3 densification cycles depending on the fiber and manufacturing parameters. This is in good accord with the principles of fracture mechanics. By densification the structural stability and the capability of load transfer between fiber and matrix is improved, the interlaminar shear strength increases, thus the composite can carry a higher load. By progressive densification of the matrix, the difference between Young's moduli of fiber and matrix and the elastic mismatch decrease. The critical interface energy reaches its minimum if the moduli are equal. Moreover

the stress on the fibers during manufacturing due to matrix shrinkage leads to a pre-damaging of the composite which is higher at higher calcination temperatures.

## 5. Acknowledgements

We like to thank the Deutsche Forschungsgemeinschaft DFG for financing this study in the programme of emphasis "Precursorkeramik", grant no. GA 589/2-4.

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