

# **Influence of curing conditions of polysiloxane ceramic precursors on mechanical properties of ceramic matrix composites**

Teresa Gumula, Stanislaw Blazewicz

AGH - University of Science and Technology, Faculty of Materials Science and Ceramics  
Department of Biomaterials, Al. Mickiewicza 30, 30-059 Krakow, Poland

## **Abstract**

The aim of this work was to obtain ceramic matrix composites reinforced with carbon fibres via polymer impregnation technique and to investigate the influence of curing conditions on mechanical properties of ceramic matrix composites. Due to presence of ceramic matrix, such composites have better oxidation resistance, and can be considered as construction elements working at elevated temperature in an oxidative atmosphere. They have also interesting electrical properties and can be applied as heating resistors.

Polysiloxane resins, produced by Lucebni zavody, Kolin (Czech Republic) were used as the matrix precursors. HTS 5131 carbon fibres (Tenax-J) as reinforcing material were used. The unidirectional composite samples were manufactured according to the liquid impregnation procedure. Polymer-based composite samples prepared in different way (curing under pressure of 0.01 MPa (PMCs 0.01) and 0.9 MPa (PMCs 0.9)) were subjected to thermal treatment up to 1000°C for a total time of 24 hours in order to receive silicon oxycarbide matrix composites (CMCs).

Mechanical properties, including bending strength, Young's modulus and interlaminar shear strength (ILSS) of composite samples after each stage of heat treatment (curing, HT at 1000°C) were studied. It was found that for polymethylphenylsiloxane-based composites bending strength and ILSS values depend on curing conditions. For polymethylsiloxane-based composites bending strength do not depend on the curing conditions. However, ILSS values for PMCs and CMCs based on polymethylsiloxane resin cured under pressure of 0.9 MPa are higher in comparison to samples cured under pressure of 0.01 MPa.

## **1. INTRODUCTION**

Silicon – containing polymers are being extensively used as ceramic precursors. By controlled heat treatment of those polymers various silicon - based ceramics materials can be obtained. Pyrolysis of crosslinked silicon-contained polymers at 400-1000°C, in an inert atmosphere, leads to formation of silicon oxycarbide glass-like material (containing various ratio of Si:O:C), at higher temperatures appeared nano-sized crystals, and above 1500°C SiC crystallizes [1-4]. Their chemical composition, structure, microstructure depend on the precursor type and pyrolysis conditions, especially on final heat treatment temperature. First experiments concerning receiving ceramic materials from silicon-containing polymers began Yajima. He utilized polycarbosilanes as the precursor for silicon carbide. This process is currently commercially applied for receiving Nicalon fibres [5, 6].

The use of polymer precursors for preparation of ceramic matrix composites by polymer impregnation technique allows developing simple and economical methods for producing ceramic matrix composites. In comparison with well-known methods, such as sintering of ceramic powders and the fibres, hot pressing or hot isostatic pressing [7], polymer impregnation technique has several advantages. The major advantages of this method are: reduction of impurities in the final product, generation of novel material that cannot be produced by conventional method (structure, microstructure and properties of ceramic phase depend on polymer precursor and processing parameters) and low damage of fibres during processing.

Silicon containing polymers are often used as precursors of ceramic matrix composites reinforced with carbon or silicon carbide fibres [8-13]. The most important factors, that influence on the properties of ceramic matrix composites obtained from polymer precursors are: mass losses of polymer precursor during heat treatment and the presence of free carbon phase in ceramic products. Mass losses of polymer precursor should be minimized, whereas the presence of free carbon phase might influence on strength of CMCs.

The aim of this work was to determine the effect of curing parameters of various polysiloxane resins used as ceramic matrix precursor of composites. The composites were heat treated up to 1000°C. The influence of pressure applied during curing process on mechanical properties of resulting composite was studied. Moreover, processing aspects (ceramic yield, free carbon phase content in solid pyrolysis residue) of the resins used as ceramic matrix precursors were investigated.

## 2. MATERIALS AND METHODS

Polysiloxane resins produced by Lucebni zavody, Kolin (Czech Republic) were used as the matrix precursors. The resins were heat treated to 1000°C and mass residues were measured. Free carbon content was determined by thermogravimetric analysis of the mass residue heat treated to 1000°C in an oxygen atmosphere. The characteristic parameters of ceramic phases obtained after heat treatment to 1000°C is gathered in the table 1.

**Table 1.** Characteristics of cured resins after subsequent heat treatment at 1000°C

Type of resin	Ceramic yield [wt%] (thermogravimetric analysis, temperature range 20-1000°C, argon atmosphere, heating rate 10°C/min)	Free carbon content [wt%] (thermogravimetric analysis, temperature range 20-1000°C, oxygen atmosphere, heating rate 10°C/min)
L M 130 – polymethylsiloxane resin	82	0.3
L 901 - polymethylphenylsiloxane resin	85	4.6
L 4102 - polymethylphenylsiloxane resin	86	2.9
L 150 X - polymethylphenylsiloxane resin	47	9.3

HTS 5131 carbon fibres (Tenax-J) as reinforcing material were used. The unidirectional composite samples were manufactured according to the liquid impregnation procedure. Carbon roving was wrapped onto a rotating cylindrical drum in order to form a kind of tape. The carbon fibres tape was then immersed with polysiloxane solution. After drying the impregnated fibre material (monotype) was removed from the drum, cut into desired shape, laid up (stacked) in a metallic mold, in the required orientation (1D) and pressed. Such polymer-based composite samples, differed in matrix precursors, were then cured either under pressure of 0.01 MPa (PMCs 0.01) or under pressure of 0.9 MPa (PMCs 0.9), and then subjected to thermal treatment up to 1000°C, for a total time of 24 hours. In such way silicon oxycarbide matrix composite were obtained (CMCs). The characteristics of investigated composites are given in table 2. As it results from this table the volume fraction of fibres in all examined samples was comparable, whereas they differed in geometrical changes (shrinkage) caused by differences in ceramic yield of composites.

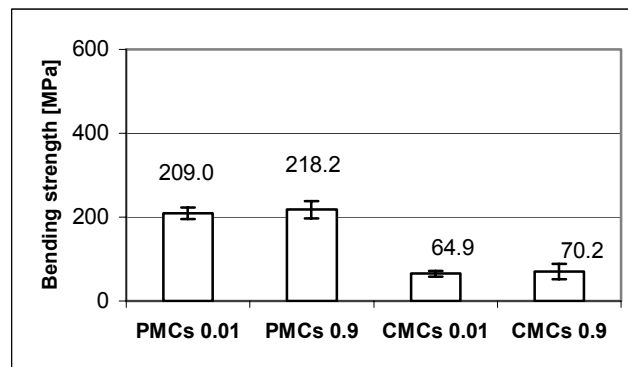
**Table 2.** Characteristic of investigated composites

Type of composite	Fiber volume fraction in PMCs [%]	Shrinkage of PMCs after heat treatment up to 1000°C [%]
C - L M 130	0.54 +/- 0.02	6.6
C - L 901	0.50 +/- 0.02	5.9
C - L 4102	0.51 +/- 0.03	5.5
C - L 150 X	0.49 +/- 0.02	19.0

To determine bending strength and Young's modulus, the composite samples were investigated in three point bending test. The ratio of the thickness to the span between loading points was higher than 16. The samples in the form of bars were loaded during the test with the rate of 2 mm/min. The interlaminar shear strength (ILSS) was determined in three point bending test under the condition that the ratio of the thickness to the span between loading points was 5. The measurements have been made on Zwick machine model - 1435. Mechanical properties of composite samples after each stage of heat treatment (curing, HT at 1000°C) were studied.

### 3. RESULTS & DISCUSSION

The bending strength of PMCs and CMCs is shown in the Fig. 1-4. It can be seen that curing conditions of PMCs based on L 4102 and L 150 X resin influences bending strength – higher pressure during curing of those composites produces higher bending strength (Fig. 3, 4). However the mechanical parameters obtained for all PMCs (Fig. 1-4) are relatively low and far from the mixture rule of 1D composites.



**Fig. 1.** Bending strength of L M 130 resin-based composites

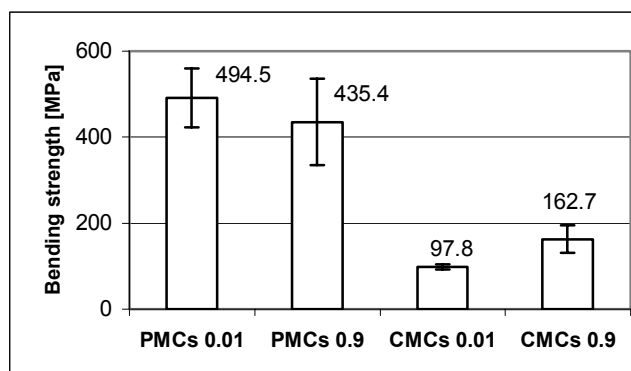


Fig. 2. Bending strength of L 901 resin-based composites

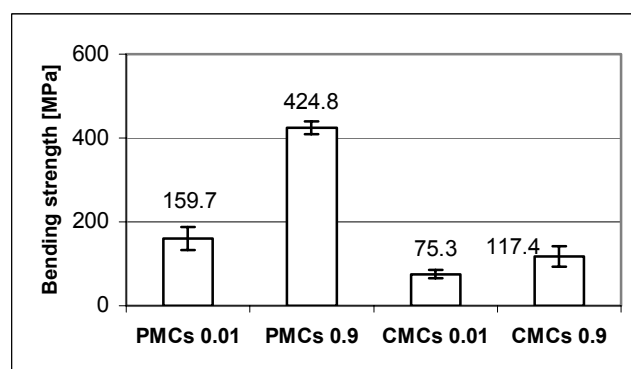


Fig. 3. Bending strength of L 4102 resin-based composites

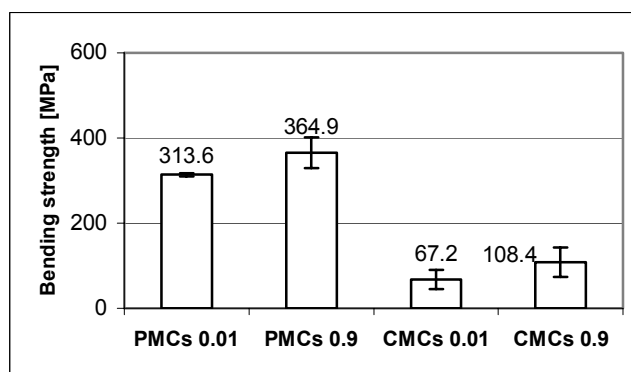


Fig. 4. Bending strength of L 150 X resin-based composites

After heat treatment of PMCs to CMCs the bending strength decreases distinctly. The changes in bending strength can be correlated with mass losses of matrix and shrinkage of composites during heat treatment. In the case of L 150 X resin-based CMCs representing the lowest ceramic yield (see table 1) and the highest shrinkage (table 2), a decrease of strength is about 4-5 times in comparison with PMCs (Fig. 4). Moreover, it was expected due to the specific characteristics of L 150 X resin (high mass losses, high shrinkage), that the resulting CMCs samples should have the lowest mechanical properties in comparison with the other types of polymer precursor used in this work (table1, table 2). It can be explained by the presence of free carbon phase in ceramic matrix. Probably, the presence of free carbon phase improves the mechanical properties of this composite. The influence of free carbon phase in ceramic matrix

on strength is also revealed by comparison of the samples differing significantly in ceramic yield and shrinkage (L M 130 and L 150 X). In spite of high differences in analysed parameters mechanical properties of those CMCs are similar (Fig. 1 and Fig. 4). Curing of PMCs under the pressure of 0.9 MPa improves the bending strength of CMCs based on polymethylphenylsiloxane resins (Fig. 2-4). On the other hand, the effect of pressure curing was not observed for the PMCs and CMCs samples obtained from polymethylsiloxane resin (Fig. 1).

The ILSS values of investigated composites are presented in the Fig. 5-8.

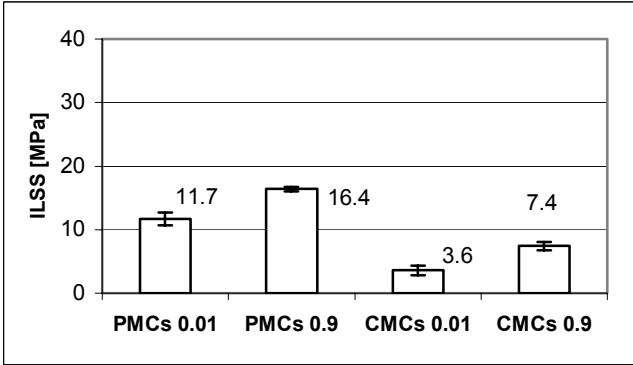


Fig. 5. Interlaminar shear strength (ILSS) of L M 130 resin-based composites

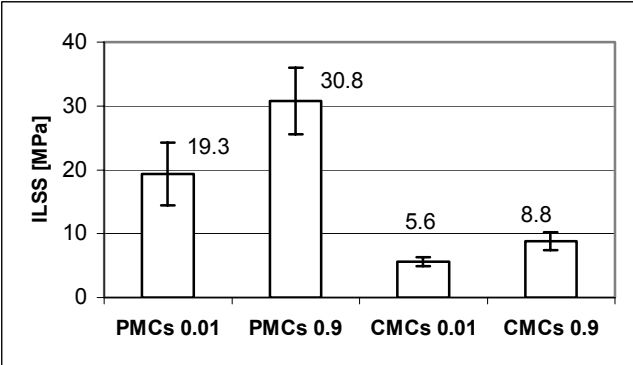


Fig. 6. Interlaminar shear strength (ILSS) of L 901 resin-based composites

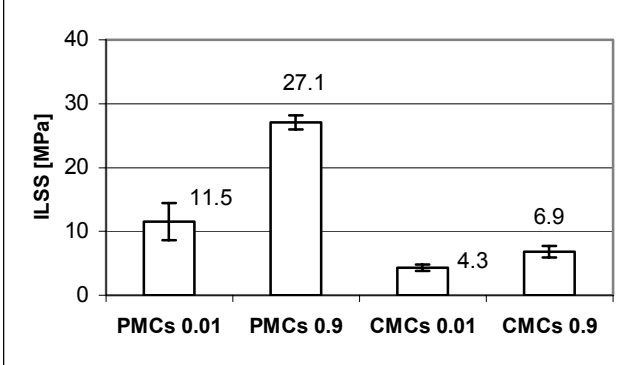
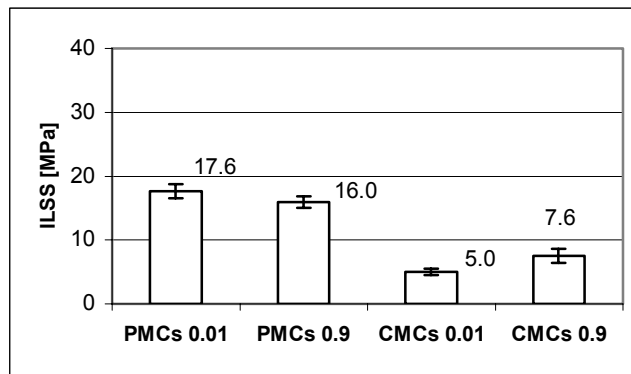


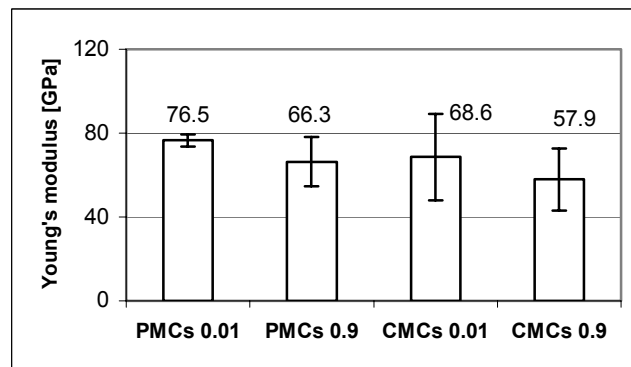
Fig. 7. Interlaminar shear strength (ILSS) of L 4102 resin-based composites



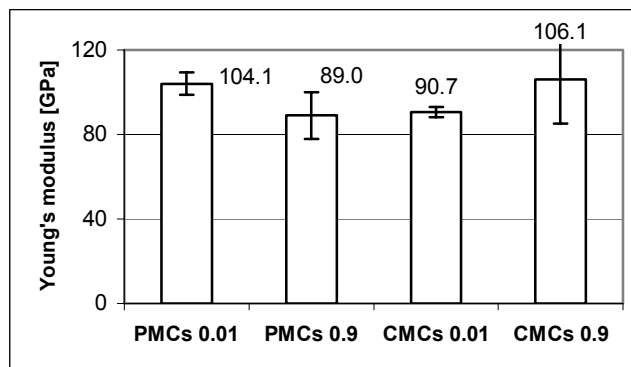
**Fig. 8.** Interlaminar shear strength (ILSS) of L 150 X resin-based composites

The effect of pressure on ILSS values is visible for PMCs based on L M 130, L 901 and L 4102 resins (Fig. 5, 6 and 7). Taking into account typical ILSS for PMCs the obtained here values are relatively low. Due to thermal decomposition of polymer matrix a decrease of ILSS value is observed. CMCs cured under the pressure of 0.9 MPa demonstrate distinctly higher interlaminar shear strength.

The diagrams in Fig. 9-12 show the Young's modulus of PMCs and CMCs. It was found that curing conditions do not influence significantly on Young's modulus not only for PMCs but also for CMCs.



**Fig. 9.** Young's modulus of L M 130 resin-based composites



**Fig. 10.** Young's modulus of L 901 resin-based composites

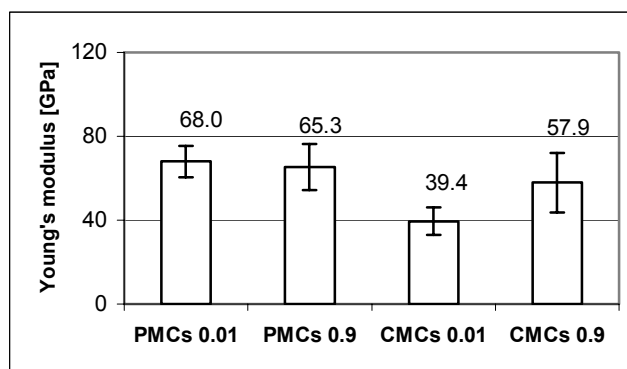


Fig. 11. Young's modulus of L 4102 resin-based composites

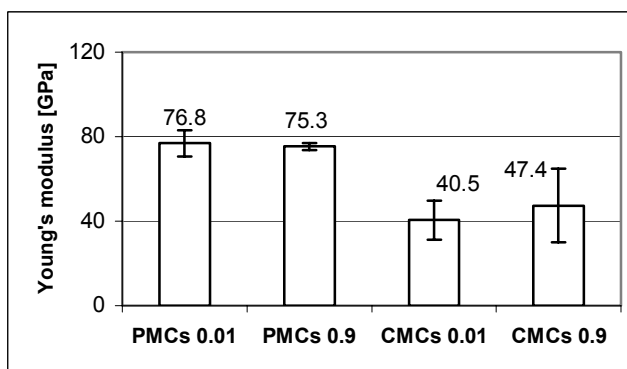


Fig. 12. Young's modulus of L 150 X resin-based composites

#### 4. CONCLUSIONS

Decreasing of mechanical properties after heat treatment of PMCs to CMCs is caused by mass losses of polymer matrices and shrinkage of composite during this process. Better mechanical properties represents the CMCs obtained from the precursors providing both higher ceramic yield during pyrolysis and containing free carbon phase in matrix.

Pressure curing modifies mechanical properties of composites. For PMCs based on polymethylphenylsiloxane polymer precursors higher pressure applied during curing produces higher mechanical properties of PMCs and subsequent CMCs.

Bending strength and Young's modulus obtained for PMCs and CMCs are low and do not fulfil the mixture rule. To obtain high mechanical properties of CMCs, polymer-based composite should have also high mechanical properties.

Further investigation of silicon-based polymer should concentrate on preparation of pure silicon carbide matrix of composite. It requires heat treatment at higher temperatures than these applied in this work.

#### ACKNOWLEDGEMENTS:

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