JOURNAL OF MATERIALS SCIENCE **39** (2004) 2239–2242

Young's modulus of ceramic matrix composites with polysiloxane based matrix at elevated temperatures

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Recent studies on processing, physical and thermal properties of Blackglas^{TM} [1–3] confirm an increasing interest in its utilization as a low-cost matrix in heat resistant composites. Blackglas^{TM} results from pyrolysis under inert conditions of a siloxane monomer polymerized with a catalyst to produce a refractory silicon oxycarbide.

Kinetics of polysiloxane polymer pyrolysis was analyzed in [4]. In our laboratory, pyrolysis products of cured polysiloxanes based on methylsilicone and methylphenylsilicone resins (made by Lucebni zavody, Kolin, Czech Republic) have recently been investigated [5]. Glassy dark materials similar to the pyrolysis products of sol-gel derived organosilicate polymers emerge by pyrolysis in nitrogen at 600–1000 °C of the polymers cured without catalyst addition. The temperature of pyrolysis roughly determines the temperature to which the material is stable in air. These results encouraged us to explore the possibility to utilize polysiloxanes as matrix precursors in manufacture of oxidation-resistant fiber reinforced composites [6, 7].

In the present study the elastic behavior of unidirectional composites with matrix derived from cured polysiloxanes and reinforced with SiC or alumina fibers (Nicalon^{TM} or Nextel^{TM}, respectively) is investigated at temperatures up to 1300 °C in order to assess limits of their potential utilization as a structural material in air environment.

The unidirectional composites were prepared by wet winding (prepreg) technique. Methylsilicone (M130) and methylphenylsilicone (L901) resins were employed as matrix precursors. The 6 mm wide prepreg layers were stacked in a heated mold and cured at 225 °C under uniaxial pressure of 1 MPa. Each batch consisted of 6 specimens processed simultaneously. The cured composites were cut to specimens 80 × 6 mm (height 1.4–2.1 mm) and pyrolyzed in nitrogen at 1000 °C (heating rate 50 K/h, 1 h soaking time at 1000 °C). In order to densify the rather porous composites they were twice impregnated with the same matrix precursor and re-pyrolyzed under the same conditions as above. Prior to measurement of flexural moduli at elevated temperatures the specimens were annealed in air to 1200 °C.

The open porosity of the specimens was measured by the water penetration method according to the ASTM-C20 standard. In order to assess the mechanical properties of the investigated materials their dynamic elastic moduli were measured at room temperature (RT) prior to the main four-point bending experiments. The dynamic tensile modulus E_{11} was determined from the basic longitudinal resonant frequency of a beam with free ends. The in-plane dynamic shear modulus G_{12} was obtained from flexural vibrations by a resonant frequency method [8]. The resonant frequencies were measured using an electrodynamic resonant frequency tester Erudite (CNS Electronics Ltd., London, UK) at frequencies up to 100 kHz.

The Young's modulus was measured in a four-point flexural arrangement (thickness to span ratio (1.5–2.0)/40) at room and elevated temperatures. A testing machine INSPEKT (made by Hegewald-Peschke, Germany) with a 5 kN load cell with high-temperature facility for flexural tests PMA 04/06 and furnace (both up to 1500 °C, made by Maytec, Germany) were employed. The sample deflection measurement was performed using a high-temperature extensometer with resolution 0.1 μm. The system transfered the positions of three reference points at the lower surface of the deflected specimen from the hot zone to the cooled inductive transducer by means of alumina rods (probe "fingers"). The deflection was measured with respect to two floating reference points located opposite the upper support rollers of the flexural fixture, which was made of SiC. In this way, measurement of deflection within the linear range of the flexural torque was maintained and, simultaneously, compensation for thermal expansion of the middle probe finger was guaranteed. The flexural modulus E was calculated from the slope of the quasilinear part of the load-deflection curve.

The tests were performed at low loads (less than 15 N), crosshead speeds 0.05, 0.2, 0.6, and 1.2 mm/min, and temperatures RT, 900, 1000, 1100, 1200, and 1300 °C. At least 5 repeated measurements were executed at each combination of speed and temperature.

Basic properties of the twice impregnated and pyrolyzed to 1000 °C specimens are given in the Table I. Figs 1 and 2 present microphotographs of the cross-sections perpendicular to the fiber axis of the composites A901 and X130, respectively.

The initial open porosity of the pyrolyzed only specimens was approximately twice that of the final value given in the Table I. Obviously, the double impregnation—pyrolysis treatment resulted in equalization of the open porosities. The volume fraction of fibers (V_f) was estimated from the

TABLE I Basic properties of the twice impregnated and pyrolyzed to 1000 °C composites

Material	Composition (fiber + matrix precursor)	Number of prepreg layers	Open porosity (%)	Volume fraction of fibers (%)
A 901	Nicalon NL202 + Lukosil 901	10	9.3	66
A 130	Nicalon NL202 + Lukosil M130	10	10.6	58
X 901	Nextel 720 + Lukosil 901	20	11.5	72
X 130	Nextel 720 + Lukosil M130	20	9.9	57

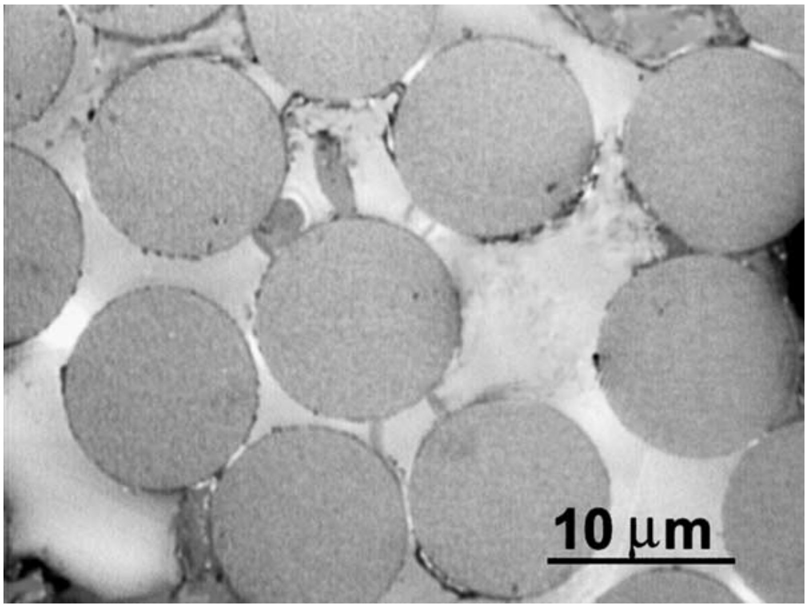

Figure 1 Microphotograph of the polished cross-section of the composite A901.

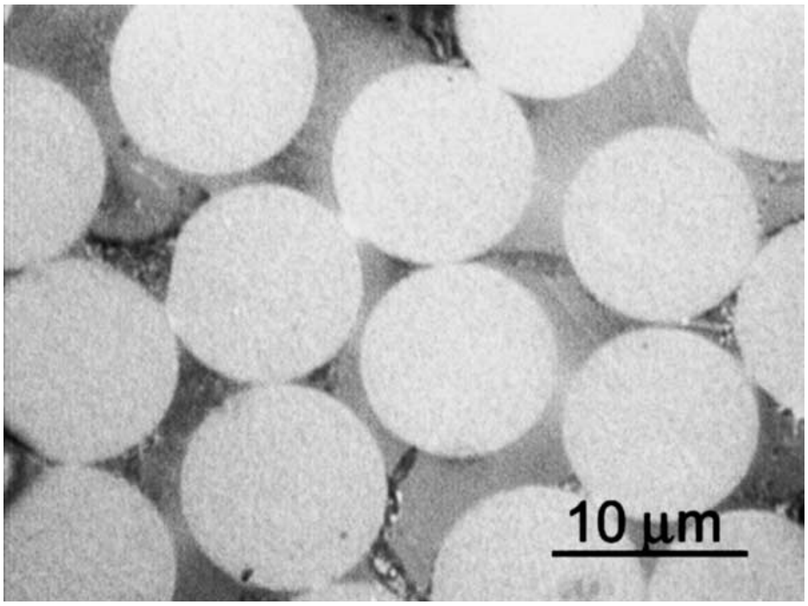

Figure 2 Microphotograph of the polished cross-section of the composite X130.

amount of fibers embedded in the specimen and its dimensions.

Dynamic tensile moduli of the composites (Table III) resemble roughly the pattern of the fiber moduli: both materials A reveal lower tensile modulus (138 and 141 GPa for A901 and A130, resp.) than the alumina fiber reinforced materials X (187 and 157 GPa for X901 and X130, resp.). This finding is in accordance with the RT tensile elastic moduli of fibers: 190 GPa (Nicalon NL202) and 260 GPa (Nextel 720) [9, 10]. The large difference between tensile moduli of Nextel-reinforced materials (X901 and X130) can be attributed to the difference in V_f in these composites (Table I). On the other hand, the in-plane shear moduli (ranging 25–35 GPa) do not match this pattern as they are probably governed by the fiber/matrix interface properties, which are not yet known to us. The open porosities of all specimens are quite similar and, consequently, they cannot be

TABLE II Weight loss of the twice impregnated and pyrolyzed to 1000 °C composites during annealing in air at 1200 °C for 2 h

Material	Relative weight loss after 1st annealing (%)	Relative weight loss after 2nd annealing (%)
A 901	8.0	≈0.0
A 130	2.2	≈0.0
X 901	4.4	≈0.1
X 130	2.4	≈0.1

TABLE III Typical values of room temperature Young's modulus

Material	Room temperature flexural Young's modulus (gpa)	Dynamic tensile Young's modulus E_{11} (gpa)
A 901	121–128	138 ± 4
A 130	124–127	141 ± 4
X 901	183–187	187 ± 5
X 130	150–165	157 ± 4

responsible for the observed variation of the dynamic moduli.

Preliminary flexural tests at the highest temperatures revealed some weight loss and dimensional shrinkage to occur during the test run. Therefore, in order to eliminate any material maturation or degradation during testing, the specimens were additionally annealed twice in air at 1200 °C for 2 h prior to performing the measurements reported hereafter. Weight losses detected after the 1st and the 2nd annealing run are given in the Table II. Eventually, all the specimens were annealed in air at 1300 °C for 2 h but, again, no weight loss was detected.

As a standard procedure, flexural measurements of Young's modulus were executed at crosshead speed 0.2 mm/min. Room temperature values roughly follow the pattern of dynamic tensile moduli (Table III), which (as already mentioned) reflects not only tensile moduli of the employed fibers but also V_f in the composite.

In order to eliminate the influence of the V_f variation and to compare thus the performance of the investigated materials the measured modulus was normalized to $V_f = 60\%$ assuming a linear dependence of modulus on V_f. Only the normalized values of the Young's modulus are presented and discussed hereafter.

The Young's modulus decreased with increasing temperature of measurement. We have established a slight influence of specimen positioning in the fixture on the absolute value of modulus. Therefore, successive test runs of the same specimen (each run lasted about 6 h and it represented insertion of the specimen into the fixture and carrying on at least 5 repeated measurements at each temperature level) yielded slightly different results the temperature trends of which, however, were mutually very similar. In order to elucidate these trends, relative values (with respect to the room—temperature value of modulus in the same run) are plotted in the graph (Fig. 3).

Obviously, all investigated composites behave similarly: there is almost no or just a very small decrease of the Young's modulus between RT and 900 °C. Its values at 1000–1100 °C do not fall under 90% of the E_{RT}. At 1200 and 1300 °C, however, a more substantial deterioration of the Young's modulus occurs to 75–80% of the E_{RT} for Nicalon reinforced composites (A901 and A130) and to 65–70% of the E_{RT} for Nextel reinforced composites (X901 and X130).

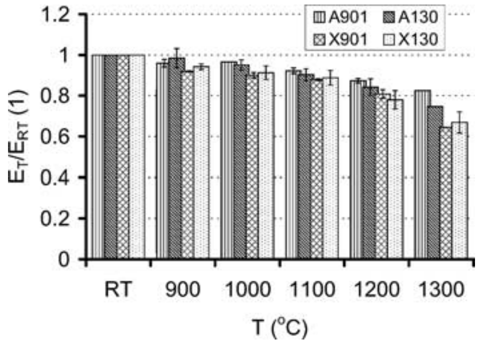

Figure 3 Average values of the ratio $E_{\mathrm{T}}/E_{\mathrm{RT}}$ (Young's modulus measured at temperature T/Young's modulus at room temperature).

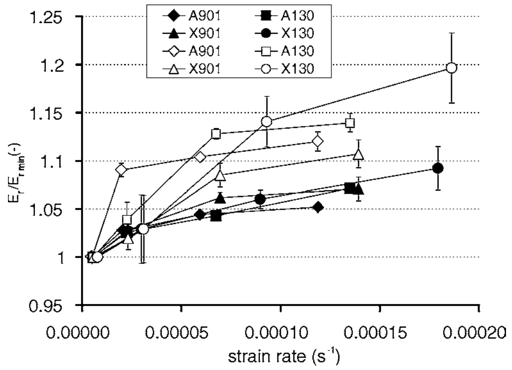

Figure 4 Relative increment of the Young's modulus at strain rate r with respect to the modulus at the lowest strain rate ($E_{\mathrm{r}}/E_{\mathrm{rmin}}$) measured at 1200 °C (heavy symbols) and 1300 °C (light symbols).

Additional high-temperature measurements of Young's modulus at alternative crosshead speeds (0.05, 0.6, and 1.2 mm/min) indicated a dependence on the strain rate. The modulus slightly increased with increasing strain rate at 1100 °C. At 1200 and 1300 °C the increment became more reproducible and reached approximately 8–10 and 15–20%, respectively, of the value corresponding to lowest strain rate (Fig. 4). Deformation response of the investigated composites deviated thus from the Hookian behavior and revealed visco-elastic features. Quantitative characterization of the phenomenon will be further studied.

It can be concluded that ceramic matrix composites with siloxane-based matrices and silicon carbide or alumina fibers are relatively stable in air up to 1300 °C as (after initial weight-loss at 1200 °C) only negligible mass loss was detected when annealing in air at 1300 °C. Their flexural Young's modulus, however, decreases remarkably above 1200 °C. Moreover, in the same temperature region, it depends also on the strain rate. These features may be limiting for prospective utilization of the investigated materials as heat resistant structural materials or—at least—they should be carefully scrutinized for applications where dynamic loading may be encountered.

Acknowledgment

The present investigation was supported by the Grant Agency of the Czech Republic, Projects no. 106/02/0177 and 106/02/P025.

References

1. M. ALLAHVERDI, W. R. CANNON and S. C. DANFORTH, *J. Amer. Ceram. Soc.* **83** (2000) 2929.
2. W. ZHAO, P. K. LIAW, R. BELARDINELLI, D. C. JOY, C. R. BROOKS and C. J. MC HARGUE, *Metall. Mater. Trans A—Phys. Metall. Mater. Sci.* **31** (2000) 911.
3. S. BRANGARAJAN, R. BELARDINELLI and P. B. ASWATH, *J. Mater. Sci.* **34** (1999) 515.
4. J. L. PLAWSKY, F. WANG and W. C. GILL, *AICHE J.* **48** (2002) 2315.
5. J. BRUS, F. KOLÁŘ, V. MACHOVIČ and J. SVÍTILOVÁ, *J. Non-Cryst. Solids* **289** (2001) 62.
6. P. GLOGAR, P. HVIZDOŠ, F. KOLÁŘ and E. RUDNAYOVÁ, in "Brittle Matrix Composites," Vol. 6, edited by A. M. Brandt, V. V. Li and I. H. Marshall (Woodhead Publ. Ltd., Cambridge and Warsaw, 2000) p. 557.
7. P. GLOGAR and E. RUDNAYOVÁ, *J. Mater. Sci. Lett.* **21** (2002) 831.
8. M. ČERNÝ and P. GLOGAR, *ibid.* **17** (1998) 425.
9. M. H. BERGER, N. HOCHET and A. R. BUNSELL, in "Fine Ceramic Fibers," edited by A. R. Bunsell and M. H. Berger (Marcel Dekker, New York, 1999) p. 242.
10. M. H. BERGER, V. LAVASTE and A. R. BUNSELL, *ibid.* p. 156.

Received 24 June
and accepted 7 October 2003