

# PROCESSING, PROPERTIES, AND PERFORMANCE OF POLYSILOXANE-DERIVED CERAMIC MATRIX IN HEAT RESISTANT COMPOSITES REINFORCED WITH R-GLASS OR FINE CERAMIC FIBRES

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## ABSTRACT

Commercially available polysiloxane resins from 3 producers were scrutinised from the viewpoint of their drying and curing kinetics. Selected resins were employed as matrix in unidirectional composites reinforced with R-glass, Nicalon<sup>TM</sup> NL202 or Nextel<sup>TM</sup> 720 fibres. The resulting polymer matrix composites were pyrolysed in nitrogen to 750°C (R-glass) or 1300°C (Nicalon, Nextel) during which the polymer matrix was gradually transformed to heat resistant silicon oxycarbide glass. Young's and shear moduli of these composites were measured at elevated temperatures. Oxidation induced damage was assessed by inspecting the microstructure.

## 1. INTRODUCTION

Ceramic matrix composites reinforced with thermally stable fibres are prospective structural materials for use in hostile (hot, oxidative) environments. Various fibre types resistant to oxidation at elevated temperatures are available commercially: R-glass and basalt fibres for medium thermal load, fine ceramic fibres like silicon carbide and oxide (e.g., alumina) fibres for high thermal load. The ceramic matrix of fibrous composites is mostly manufactured by CVD, sol-gel, or polymer pyrolysis routes. The last one is relatively simple and it has potential for manufacturing inexpensive composites by pyrolysing their "green" precursors, i.e., composites with polymer matrix, in inert (e.g., nitrogen or vacuum) environment.

In the present study, suitability of selected commercially available polysiloxane resins as preceramic matrix precursors was pursued with attention to their processing properties which are important for successful making the prepreg and moulding the composite (e.g., drying and cross-linking kinetics). Various polysiloxane resins made by Lucebni zavody Kolin (Czech Republic), Silikony Polskie (Poland), and Dow-Corning (USA) were scrutinised and some of them also utilised as a matrix in composites reinforced unidirectionally with R-glass, Nicalon<sup>TM</sup> NL202 or Nextel<sup>TM</sup> 720 fibres.

**Table 1.** Investigated polysiloxane resins.

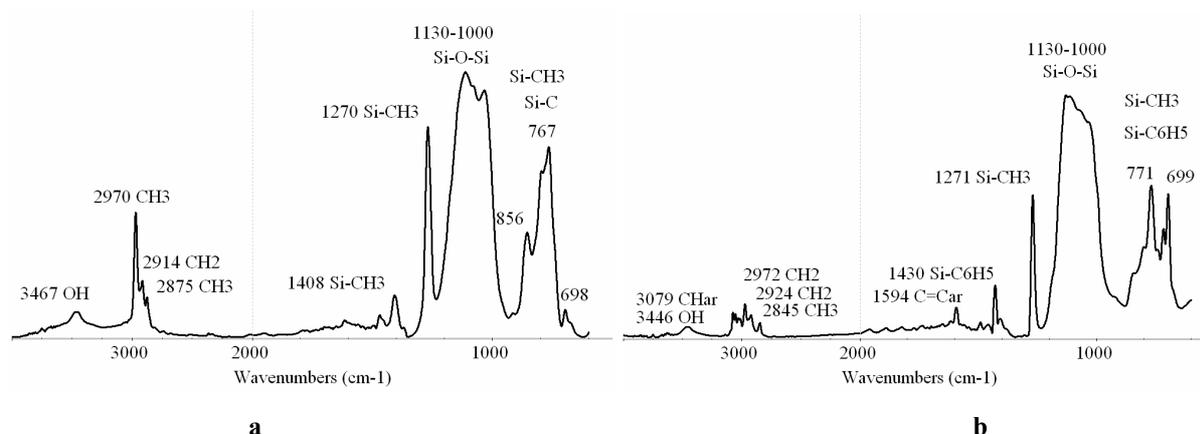
Resin	Trading name	Producer	Type	Solvent
1	Lukosil 901	Lucebni zavody, Kolin, Czech Republic	methylphenyl	toluene
2	Lukosil M130		methyl	xylene
3	Silak® M101	Silikony Polskie, Nowa Sarzyna, Poland	methyl	xylene, cyclohexanol
4	Silak® 032		methylphenyl	xylene
5	Sarsil® H-50		methyl	naphtha
6	Dow Corning® 208	Dow Corning Corporation, Midland, MI, USA	propylphenyl	xylene
7	Dow Corning® 804		methylphenyl	toluene
8	Dow Corning® 805		methylphenyl	xylene

## 2. CHARACTERISATION OF THE RESINS

The investigated polysiloxane resins are listed in Table 1.

An attempt was made to characterise semiquantitatively the studied resins by occurrence in them of groups decisive for the curing kinetics and for the thermal stability of pyrolysed polysiloxanes (silicon oxycarbide glasses). It was found in [1] that presence of phenyl groups in the precursor resin leads to a higher proneness to oxidation of the pyrolysis product due to large clusters of a free carbon phase.

Infrared spectra of the resins were measured on thin films deposited onto a KBr window using a FTIR spectrometer Nicolet 740. The absorption spectra contain distinct bands corresponding to hydroxyl groups ( $3800 - 3400 \text{ cm}^{-1}$ ), stretching vibrations of aliphatic and aromatic C-H bonds ( $3100 - 2800 \text{ cm}^{-1}$ ), and other stretching and deformation vibrations. Fig. 1 presents typical IR spectra of aliphatic and aromatic polysiloxanes.



**Fig. 1.** Infrared absorption spectra of  
a) polymethylsiloxane resin #2, b) polymethylphenylsiloxane resin #1.

In Table 2, the 1<sup>st</sup>, 2<sup>nd</sup>, and 3<sup>rd</sup> columns describe relative contributions (i.e., percentage fractions of the absorption band area) to the absorption due to silanol groups, aliphatic and aromatic bonds, respectively.

**Table 2.** Semiquantitative structure parameters of polysiloxane resins  
(the resins are lined up by their increasing aromaticity).

Resin	% OH <sup>a</sup>	% CH <sub>ar</sub> <sup>a</sup>	% CH <sub>al</sub> <sup>a</sup>	A <sub>CHar</sub> /A <sub>CHal</sub>	I <sub>1430</sub> /I <sub>1260</sub> Si-C <sub>6</sub> H <sub>5</sub> /Si-CH <sub>3</sub>	I <sub>2930</sub> /I <sub>2965</sub> CH <sub>2</sub> /CH <sub>3</sub>
2	61.5	0.0	38.5	0.00	0.00	0.32
3	74.5	0.0	25.5	0.00	0.00	0.76
5	69.2	0.0	30.8	0.00	0.00	0.63
6	87.2	3.2	9.6	0.37	3.82 <sup>b</sup>	0.63
4	51.8	16.0	32.3	0.48	0.75	0.60
7	92.0	3.2	4.7	0.71	1.21	0.13
1	61.0	16.0	23.0	0.77	0.32	1.04
8	64.5	23.2	12.3	2.10	0.94	0.21

<sup>a</sup> – Relative fraction of the absorption band area of hydroxyl groups, aromatic and aliphatic C-H bonds.

<sup>b</sup> – The value is influenced by the presence of propyl groups.

Aromaticity (i.e., the relative occurrence of aromatic CH bonds) is given by the band area ratio  $A_{\text{CHaromatic}}/A_{\text{CHaliphatic}}$ , while the ratio of phenyl/methyl groups is expressed by the relative intensity  $I_{1430}/I_{1260}$  of Si-C<sub>6</sub>H<sub>5</sub> and Si-CH<sub>3</sub> vibrations. While the #2, #3, and #5 resins contain no aromatic groups (Table 2) the other resins reveal aromaticity in some degree (maximum aromaticity is detected in the #8 resin), and the content of silanol groups in the #6 and #7 resins prevails over the others.

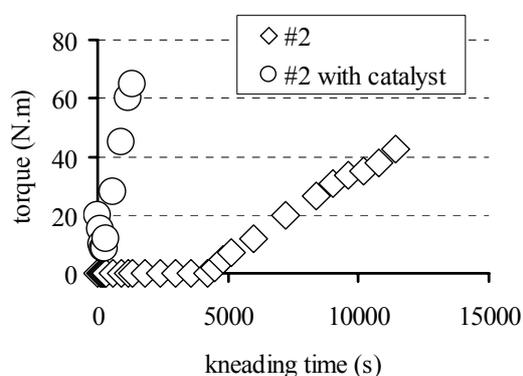
### 3. PROCESSING OF THE RESINS

Removal of the solvent is a prerequisite for curing of the resin solutions as the bubbles of the evaporating residual solvent can cause technological problems. The rate of removal for the given solvent depends – besides its concentration and ambient conditions – on the thickness of layer, which is an important factor in the prepreg technology of composite manufacturing. After a week-long drying the equilibrium residual content of the solvent span 0 – 3.1 and 3.1 – 8.5wt.% for 0.2 mm and 2 mm thick layer, respectively (Table 3).

**Table 3.** Drying kinetics of polysiloxane resin solutions.

Resin	Solvent concentration (%)	Time (h)	Layer thickness (mm)	
			0.2	2.0
			$\Delta m$ (%)	
1	30	20	25.7	20.5
		143	27.0	23.4
2	50	22	48.2	44.8
		145	48.6	46.9
3	38	29	31.0	22.8
		294	34.9	29.5
4	50	24	47.9	44.0
		145	48.3	46.9
5	43	25	38.9	22.2
		145	40.4	35.0
7	35	23	34.4	29.8
		168	35.0	32.6

Thermo gravimetric analysis of the dried specimens reveals a higher weight deficit of the thicker ones, which confirms the presence in them of imperfectly removed solvent.



**Fig. 2.** Curing of the resin #2 in the Brabender plastograph.

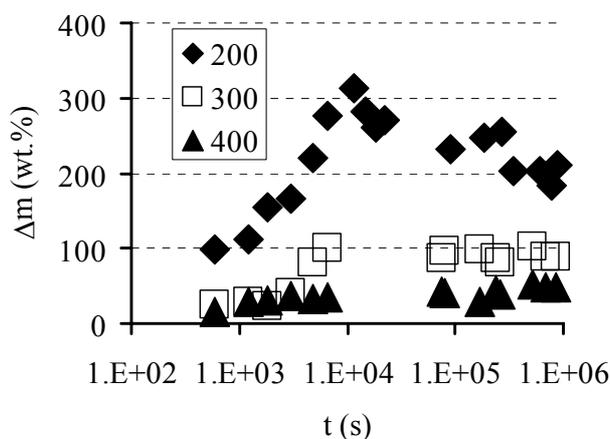
Curing of the dried resin specimens was monitored by recording the torque  $M$  using the Brabender plastograph. The  $M$  of the resin #2 during its isothermal curing at 180°C, as well as that of the resin containing 1% of the C61 catalyst (Lucebni zavody, Kolin) is plotted in Fig. 2. Obviously, the catalyst-added resin is cured too fast to reliably remove the solvent. Only catalyst-free curing was therefore pursued in this study.

Process of polycondensation at temperatures 200 - 400°C was monitored by determining the content of insoluble fractions in an initially fully soluble resin (Table 4). The specimens treated at 200°C contain various amount of gel (from *zero* for the resins #5 and #7 to 33.7 wt. % for #2 resin). Among the specimens treated to 400°C those containing only methyl groups (i.e., #2, #3, and #5) clearly prevail in cross-linking conversion over the others.

**Table 4.** Content of gel in polysiloxane resins after 1 h heat treatment in nitrogen (extraction at 25°C in toluene, duration 667 h).

Resin	Heat treatment temperature (°C)		
	200	300	400
Gel content (wt. %)			
1	-	85.5	93.2
2	33.7	81.3	98,6
3	14.0	98.2	99.5
4	8.5	69.6	72.9
5	0	88.8	97.7
7	0	85.2	90.9

The mass variation during soaking in toluene of the resin #2 is plotted in Fig. 3. The initial strong swelling of the specimen heat-treated at 200°C is followed by the sol extraction. On the other hand, the specimens treated at 300 and 400°C contain already a high amount of the cross-linked product and their swelling is low.



**Fig. 3.** Initial stage of swelling for the resin #2 heat-treated to 200 - 400°C in nitrogen.

#### 4. MANUFACTURE OF FIBROUS COMPOSITES

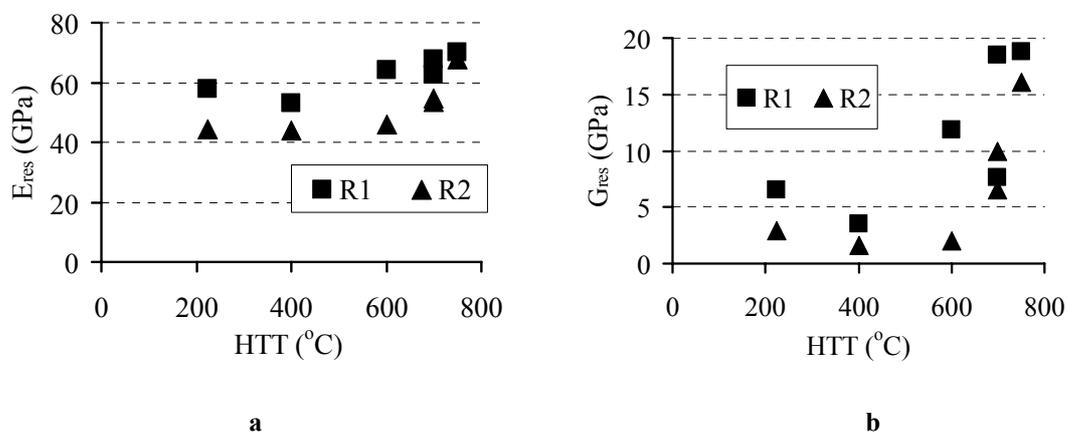
Selected resins were employed as polymer precursors for matrices of unidirectional composites. The choice of reinforcement resulted from the presumed upper temperature limit of the composite utilization. R-glass rovings (Stratifil RC10 800 with silane type sizing P109 made by Saint-Gobain Vetrotex) were designated for temperature up to 750°C while Nicalon™ NL202 (made by Nippon Carbon) or Nextel™ 720 (made by 3M) rovings were appointed for temperatures up to 1200°C. The composite batches are labelled by a combination of a character (R, A, or X for R-glass, Nicalon, or Nextel, respectively) and a digit (1 for Lukosil 901 etc., see Table 1): e.g., A1 stands for the Nicalon reinforced composite with the Lukosil 901 matrix.

The composites were manufactured in lab using a wet-winding (prepreg) technique. The amount of resin soaked into the roving was controlled by adjusting its viscosity and the gap between Teflon rollers to yield approximately 45 wt.% of resin in the dried prepreg. Several (8 – 12) prepreg sections (width 4 mm) were stacked in a heated mould and cured after compressing to the thickness 1.2 – 1.5 mm.

It follows from the above results that the curing at 200°C is not sufficient for complete cross-linking of the investigated resins. Postcuring at 225°C for 2 - 4 hours yielded specimens of polymer matrix composites, which were further pyrolysed in nitrogen at a rate of 50K.h<sup>-1</sup> to the target temperature, denoted hereafter as HTT (heat treatment temperature). During pyrolysis the polymer matrix was gradually transformed into a more or less anorganic matrix (silicon oxyacrbide glass), which was accompanied with release of volatiles, mass loss, and void formation. In some cases the already pyrolysed composites were densified by impregnation with the resin and repyrolysed. In this way the lack of a perfect curing of the precursor composite was – at least partly - compensated.

#### 5. COMPOSITES REINFORCED WITH R-GLASS (R1, R2, R3, AND R5)

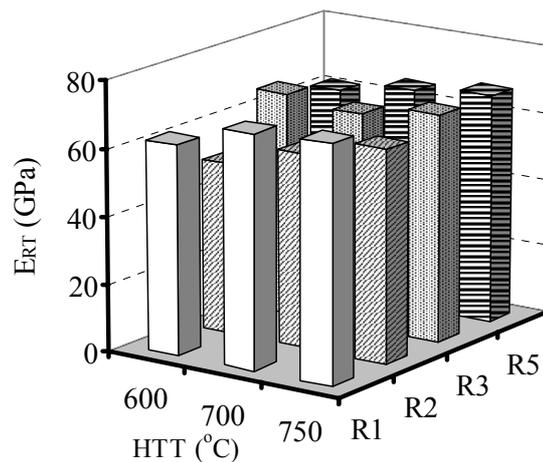
Initial transformation stages of the polysiloxane matrix to a ceramic one were monitored by measuring (at room temperature) the Young's and shear elastic moduli of R-glass reinforced composites pyrolysed to 400 - 750°C. These moduli ( $E_{res}$  and  $G_{res}$ ) were measured by means of a resonant frequency method [2]. In addition, the temperature dependence of the static Young's modulus  $E$  was measured in a 4-point flexural arrangement in air at 600 - 750°C in order to establish the upper temperature limit for the composite utilization. Moreover, the appearance of fracture surfaces after performing the room-temperature flexural test was inspected, which enabled to monitor the changing nature of the matrix due to a varying temperature of pyrolysis.



**Fig. 4.** Young's modulus  $E_{res}$  (a) and shear modulus  $G_{res}$  (b) at room temperature for 2 types of composites heat-treated in nitrogen to 225 - 750°C.

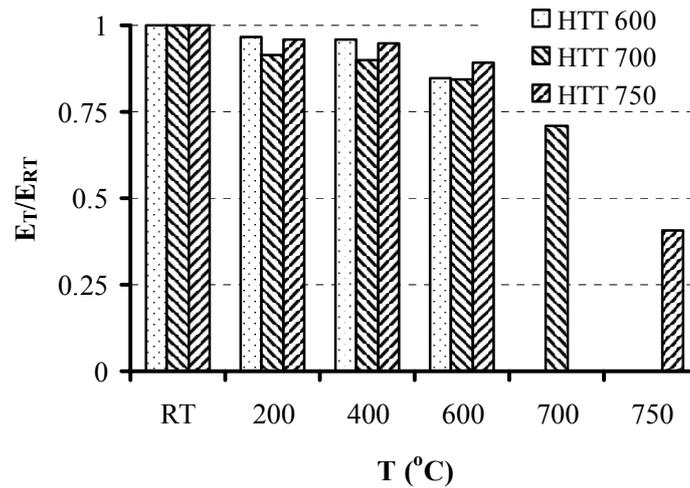
Mean values of the moduli ( $E_{res}$  and  $G_{res}$ ) measured at room temperature with 2 batches of composites either cured at 225°C or pyrolysed to HTT between 400 and 750°C are plotted in Fig. 4. The difference in volume fraction of fibres  $V_f$  (77 % and 54 % for the batches R1 and R2, respectively) is the understandable reason of the observed mutual shift of  $E_{res}$  and  $G_{res}$  values. Obviously, the shear modulus experiences pronounced changes with a minimum around  $HTT = 400 - 600^\circ\text{C}$  above which the composite material becomes sufficiently stiff in shear. On the other hand, the tensile modulus reveals only a moderately growing tendency with increasing HTT. While the Young's modulus of composite is mainly controlled by the modulus of fibres (and their volume fraction in the material), the shear modulus is governed by the properties of fibre – matrix interface and by the overall matrix integrity. Fig. 4 thus manifests a stability of the R-glass fibre and a radical polymer reconstruction during pyrolysis.

The static Young's modulus was measured in a 4-point bending arrangement (thickness to span ratio  $(1.5 - 2.0) / 40$ ). The static Young's modulus of the investigated composites measured at the room temperature ( $E_{RT}$ ) increases with increasing temperature of pyrolysis/HTT (Fig. 5). Typically, the increments reach approximately 10% between HTT 600 and 750°C, which corresponds to the gradual stiffening of the transforming matrix during pyrolysis.



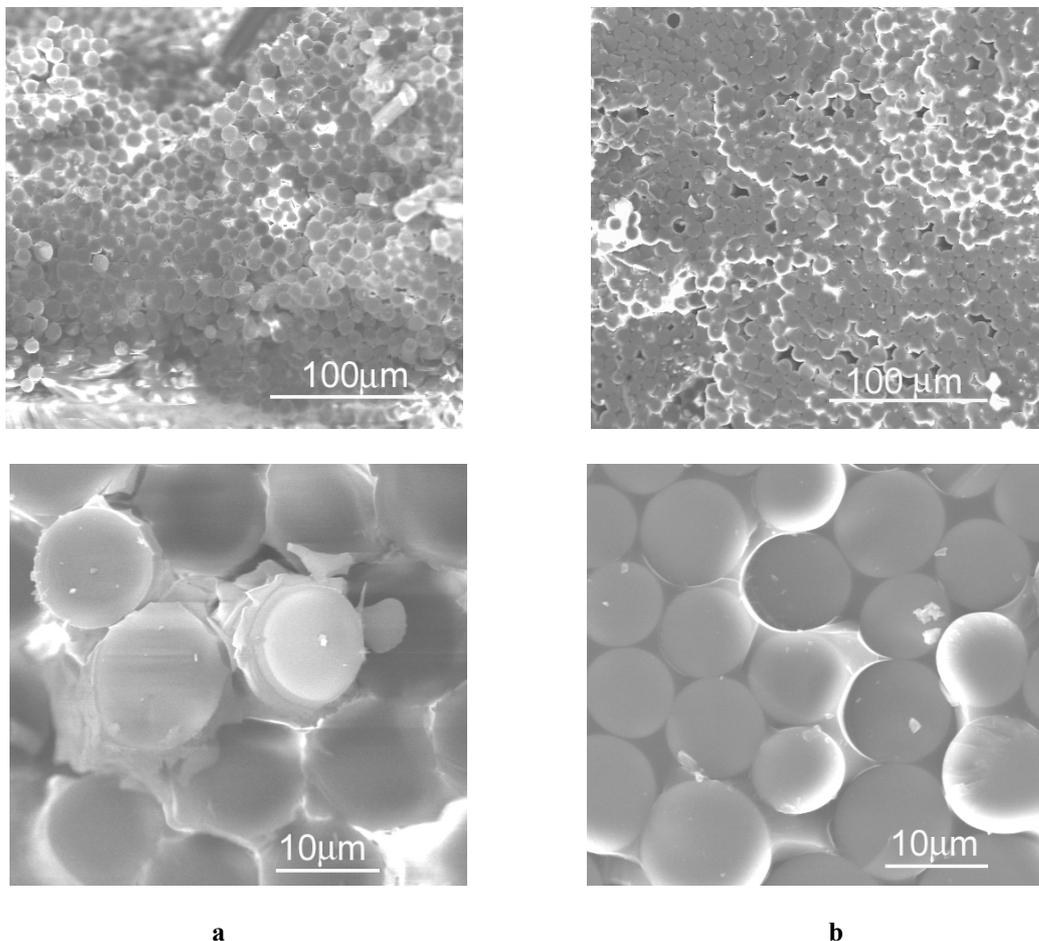
**Fig. 5.** Room-temperature Young's modulus  $E_{RT}$  of the composites pyrolysed to 600, 700, or 750°C (fibre volume fraction 77, 54, 74, and 75% for the composites R1, R2, R3, and R5, respectively).

In Fig. 6 the typical decreasing temperature dependence of these moduli ( $E_T$ ) is plotted (for the sake of clarity the plot reveals normalised values, i.e. ratios  $E_T/E_{RT}$ ). In order to check the material stability the results of consecutive tests at increasing temperatures were completed with a repeated room-temperature test, which did not differ from the initial value by more than 5%. It follows that while the HTT affects significantly the room-temperature value of the Young's modulus (Fig. 5) the rate of its decay with increasing temperature of measurement does not depend on the HTT (Fig. 6). For all composite batches R1, R2, R3, and R5 the Young's modulus at 600°C is by 10 – 12% less than its room-temperature value, and a rapid fall of the modulus takes place above this temperature. Because the softening point of the R-glass (986°C [3]) is well above the maximum reached temperature the detected decay of  $E_T$  can hardly be attributed to the first indications of fibre softening. More conceivably the matrix itself or its interface should be made responsible.



**Fig. 6.** Temperature dependence of the mean values of the static Young's modulus  $E_T$  (normalised to its room-temperature value  $E_{RT}$ ) for the composites R1 pyrolysed to HTT = 600, 700, and 750°C.

Appearance of the fracture surfaces of the specimens broken during a room-temperature 3-point flexural test (Fig. 7) depends on the HTT. A tendency towards higher brittleness of those pyrolysed to the higher temperature (HTT 750°C) is manifested by occurrence in them of extended flat areas without fracture steps while frequent fracture steps accompanied with some fibre pull-out and other energy-dissipating mechanisms can be seen in those pyrolysed to 600°C. Nevertheless, the stress-strain curves recorded during the flexural tests reveal a principally brittle fracture in all cases.



**Fig. 7.** SEM images of the fracture surfaces of the R1 composite pyrolysed to a) 600 and b) 750°C.

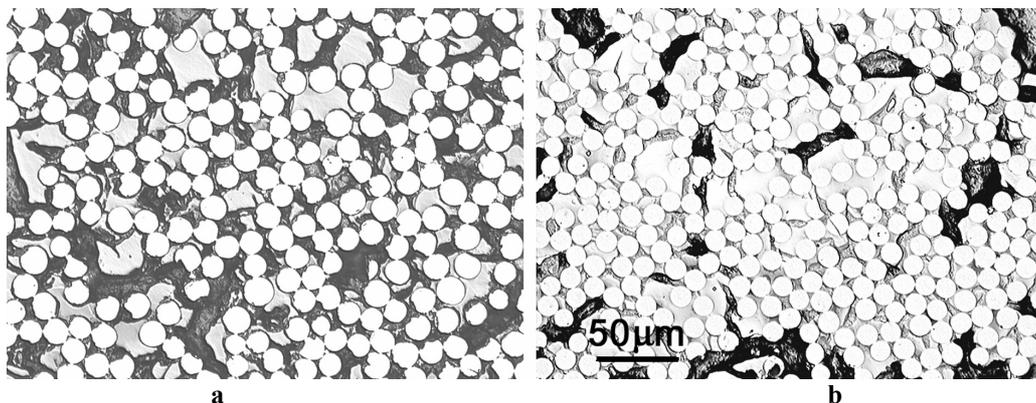
## 6. COMPOSITES REINFORCED WITH CERAMIC FIBRES (A1, A2, X1, AND X2)

Performance of the polysiloxane resins pyrolysed to 1000°C was pursued by monitoring high-temperature elastic properties of their composites reinforced with heat-resistant silicon carbide fibres Nicalon™ NL202 or alumina + mullite fibres Nextel™ 720. The composites were made by a similar process like those with R-glass reinforcement. After pyrolysis the specimens were twice subjected to the impregnation / pyrolysis cycle in order to partially heal the voids (open porosity) created by egress of volatiles. Prior to measurement of the flexural modulus the specimens were annealed in air to 1200°C (2 oxidation steps, duration 1 h each) in order to eliminate any material maturation or degradation during measurement. A higher proneness of the composites with polymethylphenylsiloxane-based matrix #1 to oxidation-induced damage if compared to their polymethylsiloxane counterpart #2 is obvious from the Table 5. Eventually, all the specimens were annealed in air at 1300°C for 2 hours but no additional weight loss was detected.

**Table 5.** Weight loss of the composites during annealing in air at 1200°C.

Material	Relative weight loss after 1 <sup>st</sup> annealing (%)	Relative weight loss after 2 <sup>nd</sup> annealing (%)
A1	8.0	0.0
A2	2.2	0.0
X1	4.4	0.1
X2	2.4	0.1

Fig. 8 displays the differences in the matrix appearance in the composites subjected to oxidation at 1200°C. It is apparent that the polymethylphenylsiloxane based matrix in the A1 composite suffers from more intense degradation than the polymethylsiloxane based one in the X2 composite. Splitting of the initially continuous matrix to segments is perhaps one of the mechanisms leading to the observed by us decrease of the shear modulus after composite oxidation [4] which reveals similar sensitivity to the type of initial resin: the decrease of shear modulus after oxidation is significantly higher with the A1 composite than with the X2.



**Fig. 8.** Polished cross-sections of the composites A1 (a) and X2 (b) after 2 oxidation steps at 1200°C.

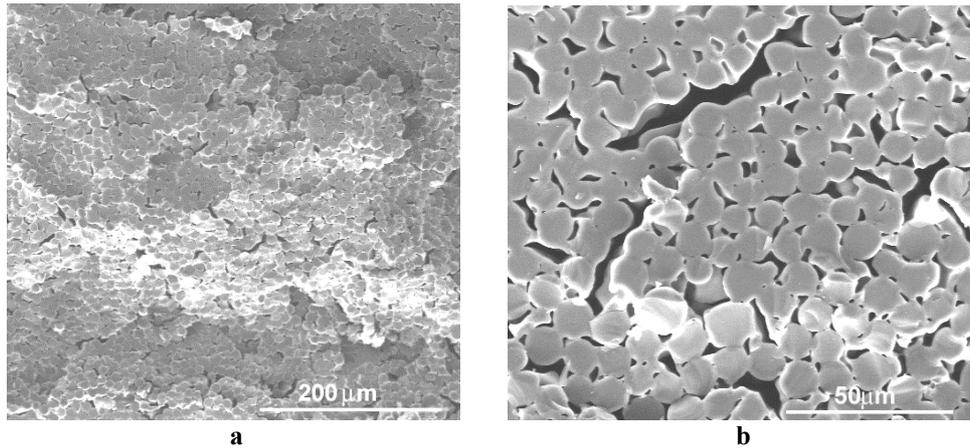
At room temperature, the values of both 4-point bending (static) and Young's (from resonant frequencies) moduli (Table 6) follow roughly the pattern of the tensile moduli and – in case of the Nextel reinforced composites – also of the volume fractions of fibres.

**Table 6.** Typical values of room temperature Young's modulus.

Material	Volume fraction of fibres (%)	Tensile modulus of fibres (GPa)	Young's modulus (GPa) measured by	
			4-point bending ( $E_{RT}$ )	resonant frequency ( $E_{res}$ )
A1	66	190	121 – 128	138 ± 4
A2	58	190	124 – 127	141 ± 4
X1	72	260	183 – 187	187 ± 5
X2	57	260	150 – 165	157 ± 4

When measured in air at temperatures up to 900°C the flexural modulus remains almost constant. A slight decrease occurs at 1000 - 1100°C but the modulus does not fall under 90 % of the  $E_{RT}$  value. At 1200 and 1300°C, however, a substantial deterioration of the Young's modulus occurs: it falls to 75 – 80 % of the  $E_{RT}$  for the Nicalon- reinforced composites (A1 and A2) and to 65 – 70 % of the  $E_{RT}$  for the Nextel- reinforced ones (X1 and X2). Moreover, in the same temperature region, the flexural modulus depends also on the strain rate [5].

At 1300°C the mean values of the 3-point bending flexural strength reach 200 – 220 MPa for the A1 and X1 composites and 170 MPa for the A2 and X2 ones. The composites reveal a brittle flexural fracture both at 900°C and 1300°C (Fig. 9).

**Fig. 9.** SEM images of fracture surfaces of the composite A901 fractured at a) 900°C, b) 1300°C.

## 7. CONCLUSIONS

Polysiloxane resins can be used as matrix precursors for heat resistant composites. From the viewpoint of the composite manufacture their curing without addition of a catalyst is preferred. The polycondensation at 200°C is incomplete which, however, is at least partly compensated by the process of pyrolysis (in nitrogen) that is used in manufacture of composites reinforced with R-glass, Nicalon or Nextel fibres. The silicon oxycarbide glass matrix, which is formed gradually above 600°C, is for the polymethylsiloxane precursor relatively stable in air up to the pyrolysis temperature but the heat resistance of polymethylphenylsiloxane derived matrix is less. The Young's modulus of the composites is governed by the reinforcing fibres, the shear modulus is a measure of the matrix integrity and it monitors both the transformation of the polymer to a ceramic and the oxidation-induced damage to the matrix.

## ACKNOWLEDGEMENTS

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