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

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Eight commercially available polysiloxane resins from 3 producers in the Czech Republic, Poland, and the U.S.A. were scrutinised by considering their weight loss after pyrolysis in inert atmosphere to 1200°C. For polymethylsiloxane resins the loss did not exceed 14 % while for polymethylphenylsiloxane ones it amounted to 20, even 30 %. Selected resins were used as matrix precursors in laboratory manufacture of ceramic matrix composites according to a polymer pyrolysis route. Rovings of continuous R-glass (Vetrotex Saint Gobain), or Nicalon NL202 (Nippon Carbon) and Nextel 720 (3M) fine ceramic fibres were used as unidirectional reinforcement of composites pyrolysed up to 750°C or 1000°C, respectively. Initial transformation stages from a polymer to a ceramic matrix were monitored by measuring the dynamic Young's and shear moduli, which yielded a pronounced minimum of the shear modulus for composites pyrolysed to 400-600°C manifesting a radical polymer reconstruction in this temperature region. The temperature dependence of the static Young's modulus is almost flat up to 600°C or 1000°C for composites reinforced with R-glass or ceramic fibres, respectively; at higher temperatures, however, a rapid fall of modulus takes place. Microscopic observation of the composites subjected to 2 h oxidation in air at 1200°C revealed that the polymethylphenylsiloxane-based matrix is more prone to damaging than its polymethylsiloxane counterpart. The observed splitting after oxidation of initially continuous matrix to segments is accompanied by a decrease of the shear modulus.

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.

Various polymers have been used as matrix precursors: polycarbosilane [1,2], silazane [3], or polysiloxane [4-8]. Several studies [9-12] focused to the commercial polysiloxane polymer Blackglas™, which possesses a high ceramic yield (82 %) upon pyrolysis, resulting in formation of a silicon oxycarbide glass. The latter is a modification of silica glass in which some pairs of oxygen atoms are substituted by carbon atoms. The pyrolysis temperature affects the properties of this glass, particularly its resistance to oxidation: increasing the pyrolysis temperature and duration increases resistance to subsequent mass loss when heated in air because of the improved formation of Si–C and Si–O bonds.

Mechanical properties of the pyrolysed composites depend on processing parameters (e.g., heat treatment temperature, densification) as well as on spatial arrangement and nature of reinforcing fibres. For composites with the polysiloxane-derived matrix reinforced with unidirectionally arranged Tenax HTA 5411 carbon fibres [4] the 4-point flexural strength and the Young's modulus were 248-413 MPa and 143-168 GPa, respectively, after pyrolysis to 750°C but only 142-252 MPa and 64-122 GPa, respectively, after pyrolysis to 900°C (the range of values corresponds to 0-2 densification cycles).

In the present study, suitability of selected commercially available polysiloxane resins as pre-ceramic matrix precursors was pursued with attention to the amount of their pyrolysis yield. Various polysiloxane resins made by Lučební závody Kolín (Czech Republic), Silikony Polskie (Poland), and Dow-Corning (USA) were scrutinised and some of them also utilised as matrix precursors in composites reinforced unidirectionally with R-glass, Nicalon™ NL202 or Nextel™ 720 fibres.

EXPERIMENTAL

Absorption infrared spectra of the polysiloxane resins were measured using the Fourier Transform Infrared Spectrometer Nicolet 740. Thin film specimens were deposited onto a KBr window and the measurement commenced after evaporation of the solvent. The spectra were accumulated 128 times with a 2 cm^{-1} resolution.

Thermogravimetric analysis of the resins was performed using a Netzsch STA 409 apparatus at heating rate 10°C/min to 1200°C. Approximately 50 mg specimens were placed in a platinum crucible; the flow of argon was adjusted to 75 ml/min.

Specimens of unidirectionally reinforced fibrous composites were manufactured by stacking and moulding 8-12 prepreg sections (length 160 mm) consisting of 2-6 parallel roving sections soaked with the resin solution. For making the prepreg, the winding machine with a rotating drum perimeter 2 m and a μ-processor controlled step motor driving the soaking carriage was employed. The gap width between the roving leading/soaking rollers was adjusted to yield approximately a 45 wt.% content of resin in the dried prepreg. The stacked prepregs were heated and cured 4 hours at 200°C after compressing to the thickness 1.5-2.0 mm by application of a uniaxial pressure up to 1 MPa.

Treatment at 200°C is not sufficient for complete curing of the investigated resins. Further treatment at 250°C for 2-4 hours under no pressure yielded specimens of polymer matrix composites, which were pyrolysed in nitrogen at a rate of 5°C/h or 50°C/h to the target temperature, denoted hereafter as HTT (heat treatment temperature). During pyrolysis the polymer matrix was gradually transformed into a more or less inorganic matrix (silicon oxycarbide 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. The lack of a perfect curing of the precursor composite was - at least partly - overcome during the pyrolysis.

The dynamic Young's and shear elastic moduli of the pyrolysed composites (E_{res} and G_{res}) were measured at room temperature by means of the resonant frequency method [13]. The modulus E_{res} was determined from the basic longitudinal resonant frequency of a beam with free ends. The shear modulus G_{res} was obtained from flexural vibrations. The resonant frequencies were measured using an electrodynamic resonant frequency tester Erudite (CNS Electronics Ltd., London, UK) at frequencies up to 100 kHz.

The static 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 PMA-06/V6 (up to 1500°C, made by Maytec) with resolution 0.1 μm.

RESULTS AND DISCUSSION

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 elsewhere [14] that two phases are formed by a controlled pyrolysis of polysiloxanes: oxycarbide glass $SiO_xC_{1-x/2}$ and a highly condensed polyaromatic system close to carbon. The proportion of the two structures depends on the precursor type and temperature of pyrolysis. Presence of phenyl groups in the precursor resin leads to formation of large interconnected clusters of a free carbon phase, which implies a higher proneness to oxidation of the pyrolysis product.

Table 1. Investigated polysiloxane resins.

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

The IR absorption spectra of polysiloxane resins contain distinct bands corresponding to hydroxyl groups (3800-3400 cm^{-1}), stretching vibrations of aliphatic and aromatic C–H bonds (3100-2800 cm^{-1}), and other stretching and deformation vibrations.

Table 2 describes relative contributions (i.e., percentage fractions of the absorption band area) to the absorption due to silanol groups, aliphatic and aromatic bonds, respectively. Aromaticity (i.e., the relative occurrence of aromatic CH bonds) is given by the band area ratio $A_{CHaromatic}/A_{CHaliphatic}$, while the ratio of phenyl/methyl groups is expressed by the relative intensity I_{1430}/I_{1260} of Si–C$_6$H$_5$ and Si–CH$_3$ vibrations. While the resins 2, 3, and 5 contain no aromatic groups (table 2) the other resins reveal aromaticity in some degree (maximum aromaticity is detected in the resin *8*), and the content of silanol groups in the resins *6* and *7* prevails over the others.

The relative weight loss established during a thermogravimetric analysis is plotted in figure 1 for almost all studied resins (the resin *4* was omitted because the specimen reached a gel state prematurely). The resins *2*, *3*, and *5* reveal ultimate weight loss 12-14 % the major part of it being located at 650-750°C. On the other hand,
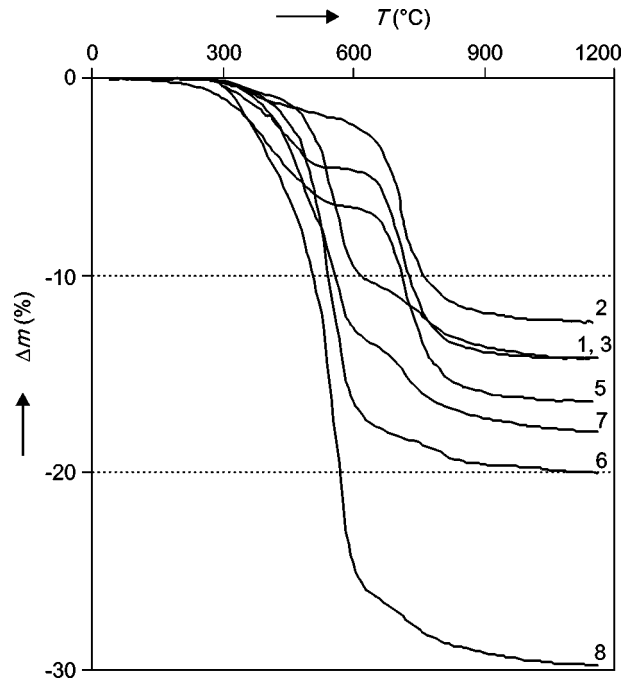

Figure 1. Relative weight loss of the dried resins 1, 2, 3, 5, 6, 7, and 8 (heating rate 10°C/min, argon).

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

Resin	% OH*	% CH$_{ar}$*	% CH$_{al}$*	A_{CHar}/A_{CHal}	I_{1430}/I_{1260} Si-C$_6$H$_5$/Si-CH$_3$
2	61.5	0.0	38.5	0.00	0.00
3	74.5	0.0	25.5	0.00	0.00
5	69.2	0.0	30.8	0.00	0.00
6	87.2	3.2	9.6	0.37	3.82**
4	51.8	16.0	32.3	0.48	0.75
7	92.0	3.2	4.7	0.71	1.21
1	61.0	16.0	23.0	0.77	0.32
8	64.5	23.2	12.3	2.10	0.94

* Relative fraction of the absorption band area of hydroxyl groups, aromatic and aliphatic C-H bonds.
** The value is influenced by the presence of propyl groups.

Table 3. Basic properties of the used reinforcing fibres.

Trading name	Producer	Composition (wt.%)	Diameter (μm)	Density (g/cm³)	Tensile strength (MPa)	Young's modulus (GPa)
Stratifil RC10	Saint-Gobain Vetrotex	58-60 SiO$_2$ 23-25 Al$_2$O$_3$ 14-17 CaO+MgO	10	2.53	3400	86
Nicalon NL202	Nippon Carbon	57 Si 32 C 11 O	14	2.55	2000	190
Nextel 720	3M	85 Al$_2$O$_3$ 15 SiO$_2$	12	3.40	2100	260

the major loss of weight of the resins *1, 6, 7,* and *8* occurs beneath 550°C and their ultimate weight loss amounts to 16-20, even 30 % (resin *8*). The poly-methylsiloxane resins *2, 3,* and *5* are the most promising for good performance at elevated temperatures because a large solid residue after pyrolysis is a prerequisite for integrity of the pyrolysed composites. They were chosen for further research together with the poly-methylphenylsiloxane resin *1*, which was included for the sake of comparison.

The 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) were designated for temperature up to 750°C while Nicalon™ NL202 or Nextel™ 720 rovings were appointed for temperatures up to 1200°C. Their basic properties are listed in table 3. 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). The constituents of particular investigated composites are listed in table 4.

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 dynamic Young's and shear elastic moduli (E_{res} and G_{res}) of R-glass reinforced composites pyrolysed up to 750°C.

Mean values of the moduli E_{res} and G_{res} measured at room temperature with two different batches of composites either cured at 250°C or pyrolysed to HTT between 400 and 750°C are plotted in figure 2. The difference in volume fraction of fibres V_f (77 % and 54 % for the batches R1 and R2, respectively) is the reason of the mutual shift of E_{res} and G_{res} values. Obviously, the shear modulus experiences pronounced changes with a minimum around HTT = 400-600°C above which the composite material becomes sufficiently stiff in shear. On the other hand, the Young's 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
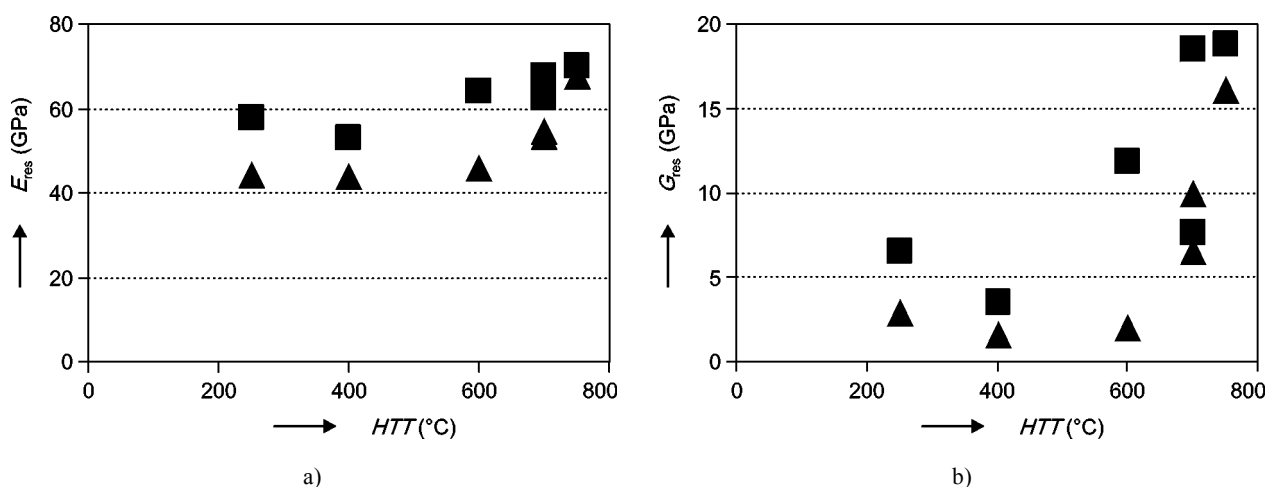

Figure 2. Young's modulus E_{res} (a) and shear modulus G_{res} (b) at room temperature for two different types of composites (■ - R1, ▲ - R2) heat-treated in nitrogen to 250-750°C.

Table 4. Labelling of the composites.

Fibre	Resin			
	1 (Lukosil 901)	*2* (Lukosil M130)	*3* (Silak M101)	*5*(Sarsil H-50)
Stratifil RC10	R1	R2	R3	R5
Nicalon NL202	A1	A2	-	-
Nextel 720	X1	X2	-	-

the properties of fibre–matrix interface and by the overall matrix integrity. Figure 2 thus manifests a stability of the R-glass fibre and a radical polymer reconstruction during pyrolysis.

The Young's moduli of the composites R1, R2, R3, and R5 measured at the room temperature (E_{RT}) increase with increasing temperature of pyrolysis 600-750°C (figure 3). Typically, the increments reach approximately 10% between HTT 600 and 750°C, which corresponds to the gradual stiffening of the transforming matrix during pyrolysis.

The temperature dependence of the static Young's modulus was measured in air up to 750°C in order to establish the upper temperature limit for the composite utilization. In figure 4 the decreasing temperature dependence of this modulus (E_T) between room temperature and 750°C is plotted (for the sake of clarity the plot reveals the values normalised with respect to the room temperature modulus E_{RT}, 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 (figure 3) the rate of its decay with increasing temperature of measurement does not depend on the HTT (figure 4). 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 [15]) 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.

It can be concluded that the resins *1*, *2*, *3* and *5* do not differ significantly in their mechanical performance up to 750°C, irrespective of their composition.

Appearance of the fracture surfaces of the specimens broken during a room-temperature 3-point flexural test (figure 5) 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.
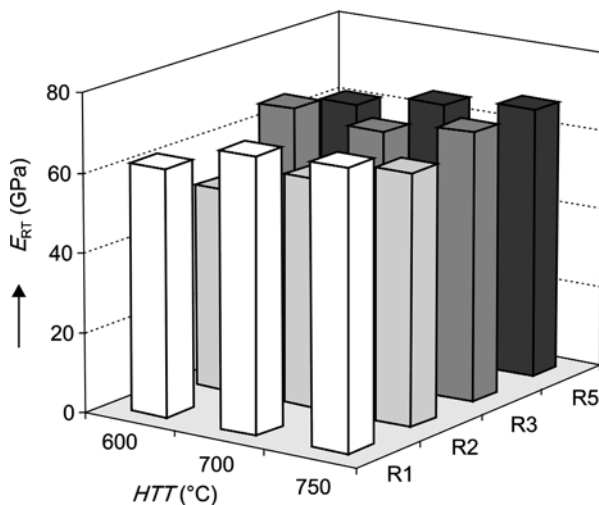

Figure 3. Room-temperature Young's modulus E_{RT} of the composites pyrolysed to *HTT* = 600, 700, or 750°C (fibre volume fraction 77, 54, 74, and 75 % for the composites R1, R2, R3, and R5, respectively).
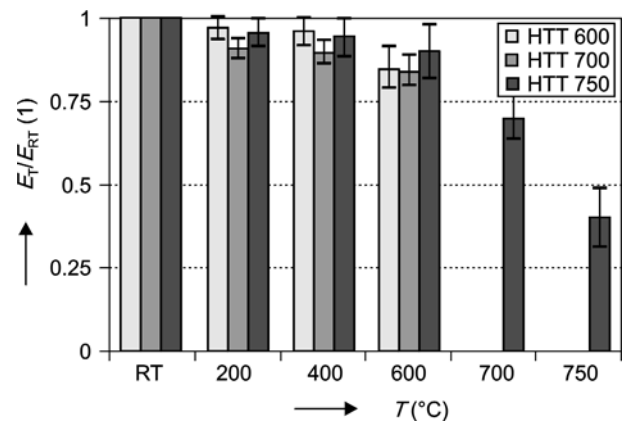

Figure 4. Temperature dependence of the mean values of the static Young's modulus E_T (normalised to its room-temperature value E_{RT}) for the composites R1 pyrolysed to *HTT* = 600, 700, and 750°C.

Table 5. Weight loss of the composites during annealing in air at 1200°C and typical values of room temperature Young's modulus.

Composite	Volume fraction of fibres (%)	Relative weight loss after 1st annealing (%)	Young's modulus (GPa) measured by	
			4-point bending (E_{RT})	resonant frequency (E_{res})
A1	66	8.0	121 - 128	138 ±4
A2	58	2.2	124 - 127	141 ±4
X1	72	4.4	183 - 187	187 ±5
X2	57	2.4	150 - 165	157 ±4

Nevertheless, the stress-strain curves recorded during the flexural tests reveal a principally brittle fracture in all cases.

Composites reinforced with ceramic fibres
(A1, A2, X1, and X2)

Performance of the pyrolysed polysiloxane resins at higher temperatures 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 to 1000°C 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 polymethyl-phenylsiloxane-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.
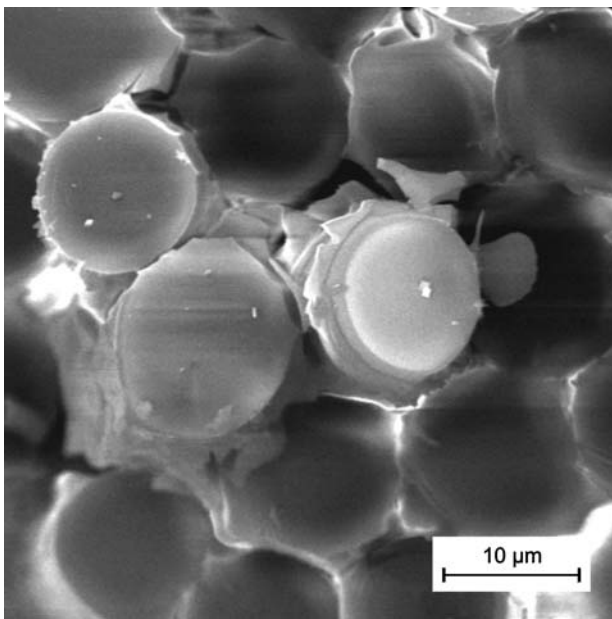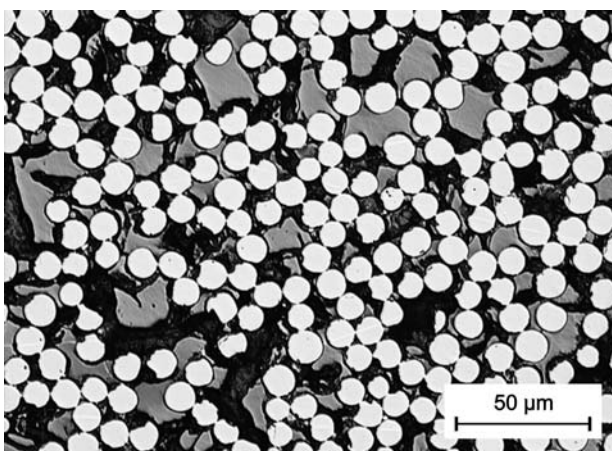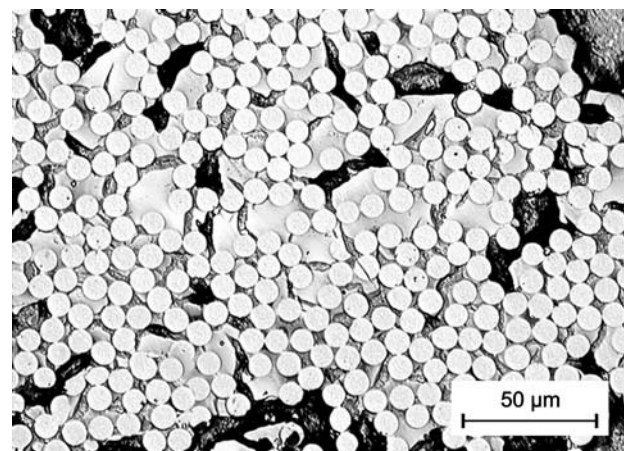

a)
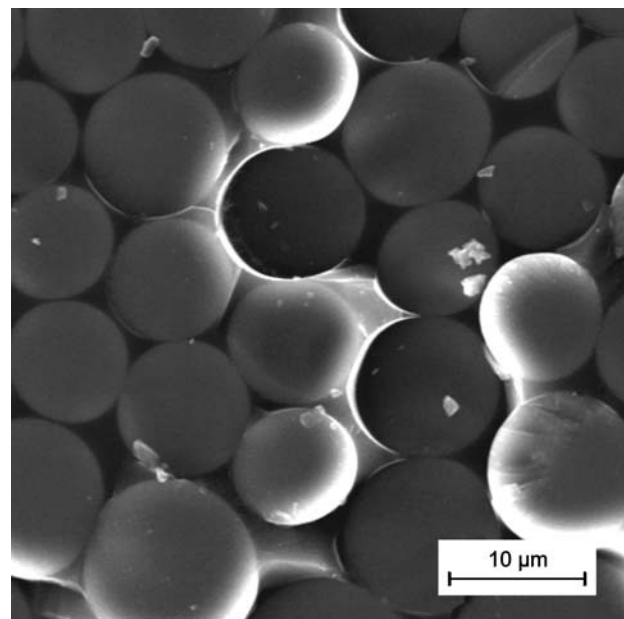
b)

Figure 5. SEM micrographs of the fracture surfaces of the R1 composite pyrolysed to a) 600 and b) 750°C.

a)

b)

Figure 6. Polished cross-sections of the composites A1 (a) and X2 (b) after 2 oxidation steps at 1200°C.

Figure 6 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 decrease of the shear modulus after composite oxidation [16] which reveals similar sensitivity to the type of initial resin: the decrease of shear modulus after oxidation is significantly higher with the A1&X1 composites than with the A2&X2 (figure 7).

At room temperature, the values of both 4-point bending (static) and Young's (from resonant frequencies) moduli (table 5) follow roughly the pattern of the tensile moduli and of the volume fractions of fibres.

The temperature dependence of the Young's modulus E_T is plotted in figure 8 (for the sake of clarity the plot reveals normalised values, i.e. ratios E_T/E_{RT}). The decrease of the Young modulus is almost negligible up to the temperature of measurement 900°C. Up to 1100°C its relative decrease with respect to the room temperature modulus does not exceed approximately 10 %. Only above 1200°C the deterioration of the modulus deviates significantly and the upper limit of the potential structural application is exceeded. Moreover, in the same temperature region, the flexural modulus depends also on the strain rate [17].

CONCLUSION

Polysiloxane resins can be used as matrix precursors for heat resistant composites. These were manufactured in laboratory by pyrolysis in nitrogen of unidirectional composites with polysiloxane matrix 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 more stable in air than the polymethylphenylsiloxane derived matrix. The Young's modulus of the composites is governed by the reinforcing fibres and is not much influenced by the oxidation. The shear modulus, however, 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.
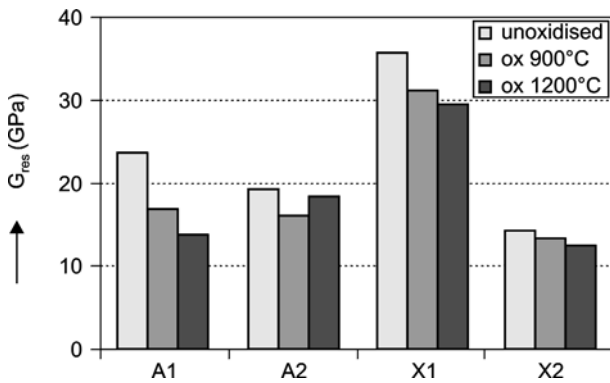

Figure 7. Mean values of the shear modulus of the specimens A1, A2, X1, and X2 (unoxidised and oxidised 1h in air at 900 or 1200°C).
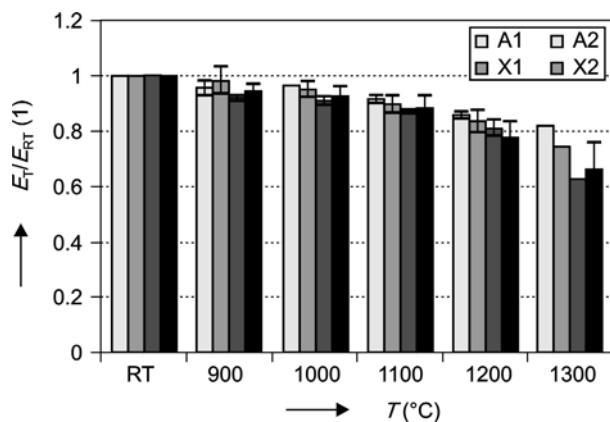
Figure 8. Average values of the ratio E_T/E_{RT} (Young's modulus measured at temperature T/Young's modulus at room temperature).

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VLASTNOSTI A CHOVÁNÍ KERAMICKÉ MATRICE ODVOZENÉ Z POLYSILOXANŮ V TEPELNĚ ODOLNÝCH KOMPOZITECH VYZTUŽENÝCH VLÁKNY R-SKLA NEBO JEMNÝMI KERAMICKÝMI VLÁKNY

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Byly stanoveny hmotnostní úbytky při pyrolýze (do 1200°C v inertním prostředí) vzorků 8 komerčně dostupných polysiloxanových pryskyřic od 3 výrobců z ČR, Polska a USA. U polymetylsiloxanových pryskyřic úbytky nepřesáhly 14 %, zatímco u polymetyl-fenylsiloxanových dosahovaly 20 až 30 %. Vybrané pryskyřice byly použity jako prekurzory matrice při laboratorní přípravě kompozitů s keramickou matricí metodou pyrolýzy polymerních kompozitů. Jako jednosměrná výztuž kompozitů pyrolyzovaných do 750°C byly použity pramence vláken R-skla (Vetrotex Saint Gobain), pro kompozity pyrolyzované do 1000°C pramence vláken Nicalon NL202 (Nippon Carbon) nebo Nextel 720 (3M). Počáteční fáze transformace polymerní matrice na keramickou byla sledována měřením dynamického Youngova a smykového modulu vzorků kompozitů. Výrazné minimum smykového modulu u kompozitů pyrolyzovaných do 400-600°C poukázalo na přestavbu polymeru v této teplotní oblasti. Teplotní závislost statického Youngova modulu je u kompozitů s R-sklem zcela nevýrazná do 600°C a u kompozitů s keramickými vlákny až do 1000°C, ale nad těmito teplotami dochází k prudkému poklesu modulu. Mikroskopické pozorování kompozitů vystavených dvouhodinové oxidaci ve vzduchu při 1200°C ukázalo, že polymetylfenylsiloxanová pryskyřice je náchylnější k poškození, než pryskyřice polymetylsiloxanová. Pozorovaný rozpad původně spojité matrice na oddělené úseky po oxidaci je doprovázen poklesem smykového modulu vzorků kompozitů.