

MICROSTRUCTURE AND MECHANICAL PROPERTIES OF HEAT RESISTANT COMPOSITES REINFORCED WITH BASALT FIBRES

PETR GLOGAR, ZBYNĚK SUCHARDA, MARTIN ČERNÝ, STEPHAN PUCHEGGER*, HERWIG PETERLIK*

*Institute of Rock Structure and Mechanics, Academy of Sciences of the Czech Republic,
V Holešovičkách 41, 182 09 Prague, Czech Republic*

**Institute of Materials Physics, University of Vienna,
Boltzmanngasse 5, A-1090 Vienna, Austria*

E-mail: glogar@irms.cas.cz

Submitted February 21, 2007; accepted June 27, 2007

Keywords: Ceramic matrix composites, Thermosetting resin, Basalt fibre, Mechanical testing, High temperature behavior

Microstructure, oxidation resistance and mechanical properties of unidirectional composites made of commercially available polysiloxane resins as matrix precursors and reinforced with continuous basalt fibres were investigated. After pyrolysis of the precursing polymer matrix composites to 600-800°C the matrix was gradually transformed to a ceramic one, which revealed low mass losses when oxidised in hot air. When subjected to a long time heat treatment in air at 700 and 800°C numerous matrix cracks emerged and plastic deformation of fibres occurred. Despite this damage of the microstructure, the elastic and shear moduli increased significantly. The increase should be attributed to structural changes of the polymer matrix transforming to a ceramic material, which prevail in their implications over the deteriorating effect of matrix cracking.

INTRODUCTION

Contemporary technologies call for new materials with specific properties. Ideally, the structural materials should be lightweight, strong, chemically and thermally stable; they should possess good mechanical properties and - last but not least - be relatively cheap. Fibre reinforced composites can fulfil many of the named requirements but none reveals these properties altogether. Consequently, a trade-off must take place.

Some composite types serve as structural materials for usage at high temperatures. Typically they can be reinforced with expensive advanced fibres (high quality carbon, boron, silicon carbide, alumina etc.), which are embedded in ceramic or metal matrices. For usage at moderately elevated temperatures (several hundreds °C) the reinforcement can be alternatively made of glass or, newly, basalt fibres. The latter outperform the glass fibres in their lower cost with allegedly comparable mechanical properties: sustained operating temperature 820°C, tensile strength 4840 MPa, tensile modulus 89 GPa, density 2.75 g.cm⁻³ (<http://www.sudaglass.com/chars.html>).

Properties and behaviour of composites reinforced with continuous or short basalt fibres have been recently studied by many authors. So, they were investigated as reinforcement in composites with concrete [1] or polymer matrix: epoxy [2], polypropylene [3-5] or phe-

nol-formaldehyde resin [6-7]. Fibre - matrix interface properties were studied in various basalt fibre - polymer matrix systems in, e.g., [2] or [3].

Due to their good thermal stability the basalt fibres can serve as reinforcement of fibrous composites manufactured by means of an additional heat treatment (i.e., partial pyrolysis in nitrogen to approximately 700-750°C) of a polymer matrix composite, which yields a ceramic matrix composite. For this purpose, selected polysiloxane resins are suitable as matrix precursors [8]. During pyrolysis, which is accompanied by release of volatiles, mass loss, and void formation, the polymer matrix is gradually transformed into an inorganic matrix (similar to heat resistant silicon oxycarbide glass).

Mechanical properties of continuous basalt fibres (CBF) at elevated temperatures have been investigated in [9]. Here, a significant loss of tensile modulus above 400°C was observed. When loaded in tension at 10 MPa and heated, a continuous elongation of the CBF tow commenced at 580-640°C (depending on the fibre type).

The aim of the present paper is to investigate the microstructure, oxidation resistance and mechanical properties of composites made of commercially available polysiloxane resins as matrix precursors and reinforced with CBF in order to determine the limit of basalt fibre reinforced materials for high temperature applications.

EXPERIMENTAL

Materials

The composite specimens were made by pyrolysis of polymer composites, which were obtained by compressing the stacks of unidirectional prepregs (length 160 mm, width 6 mm) that were soaked by the resin solution. A roving made from basalt fibre tows (RB 13 320 76, 320 tex, produced by Sudovodskoye Steklovolokno, Russia) was employed as a unidirectional reinforcement in the composite batches A - D (Table 1).

Tensile characteristics of the fibre tow were determined from 3 tests of fibre bundles performed at a gauge length of 200 mm (Table 2). The fibre diameter varies broadly around its average value 13 μm (Figure 1).

Polysiloxane resins L901 (polymethylphenylsiloxane) or M130 (polymethylsiloxane) made by Lucebni zavody, Czech Republic were used as matrix precursors. The cured at 225-250°C polymer composites were machined to specimens (length 60-65 mm, width $\approx$ 6 mm, thickness 3.5-4.5 mm), thermally treated in nitrogen (i.e., pyrolysed) to 400-800°C and eventually (in case of the specimens B and C) densified by impregnation with the same matrix precursor and re-pyrolysed. The cured composites with the L901 resin contained approximately 65 % fibres, 27 % resin and 8 % voids while those with the M130 resin 57 % fibres, 34 % resin and 9 % voids. The density of the former composites (L901) was 2.05 g/cm³ and it increased to 2.17 g/cm³ after pyrolysis at 800°C, that of the latter ones (M130) was 1.98 g/cm³ and it increased to 2.13 g/cm³.

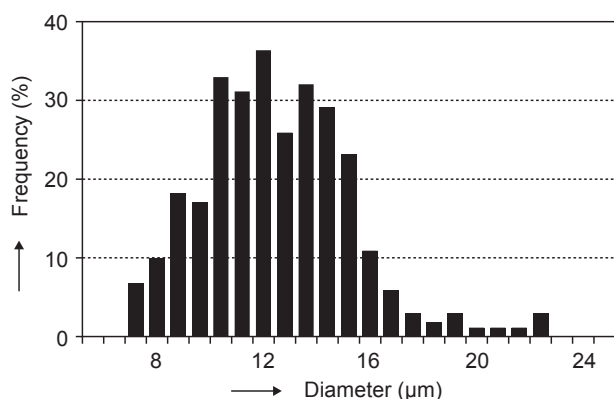


Figure 1. Distribution of fibre diameters as determined by image analysis.

After pyrolysis the specimens revealed a significant shrinkage up to 10 %, surprisingly even in length. In many cases the shrinkage (due perhaps to dimensional changes of the fibres) resulted in a deformation (twisting, bending) of the initially prismatic specimens (these specimens were excluded from further investigation). An attempt was performed to explore the behaviour of the basalt tow at elevated temperature under tensile load. The plot of its elongation under small load (Figure 2) suggests that the low-temperature thermal expansion (to $\approx$ 300°C) is followed by the lengthwise shrinkage (to $\approx$ 600°C) above which a continuous elongation takes place. This finding can be related to the microscopic observation of the shape of (initially circular) fibre cross-sections in the composite A pyrolysed to 700°C (Figure 3), which suggests a high proneness to softening of the basalt fibres at this temperature.

Another microscopic observation reveals easy breaking of the fibres when a perpendicularly propagating crack in the matrix approaches the fibre (Figures 4 and 5). It follows that for successful preparation of the

Table 2. Tensile Young's modulus and parameters of the Weibull distribution from tensile tests of basalt fibre bundles.

	I	II	III
E (GPa)	74.1	76.7	77.2
ε_0 (%)	1.071	1.047	1.122
σ_0 (MPa)	793.4	802.9	866.2
m (shape factor)	3.5	4.1	3.4

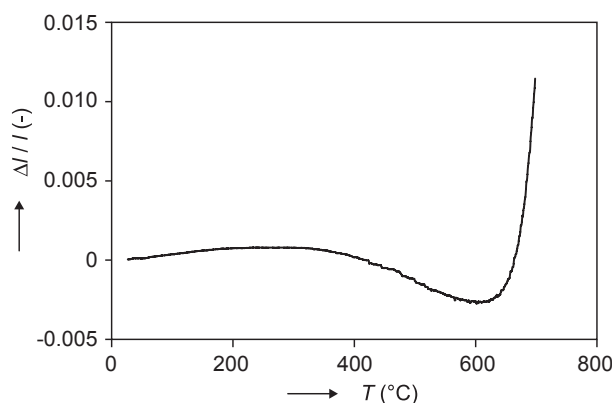


Figure 2. Plot of tensile deformation of the basalt tow at increasing temperatures (tensile stress 30 MPa).

Table 1. List of specimens.

	Matrix	Reinforcement	Pyrolysis temperature (°C)	Oxidation (°C)
A	M130	tow	400, 500, 600, 700	-
B	L901	tow	800	700, 800
C	M130	tow	800	700, 800
D	M130	tow	700	700
E	M130	fabric	700	700

basalt fibre reinforced composites a proper attention should be paid to optimisation of the processing parameters (including pressure and heating/cooling rates) in order to minimize residual stresses within the specimens.

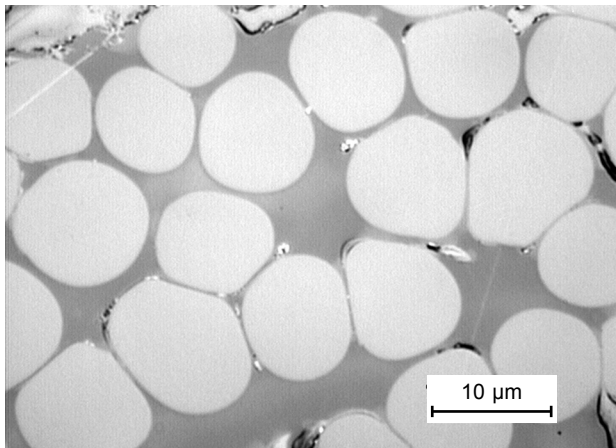


Figure 3. Cross section of the unidirectional composite A (basalt fibres + M130) pyrolysed to 700°C.

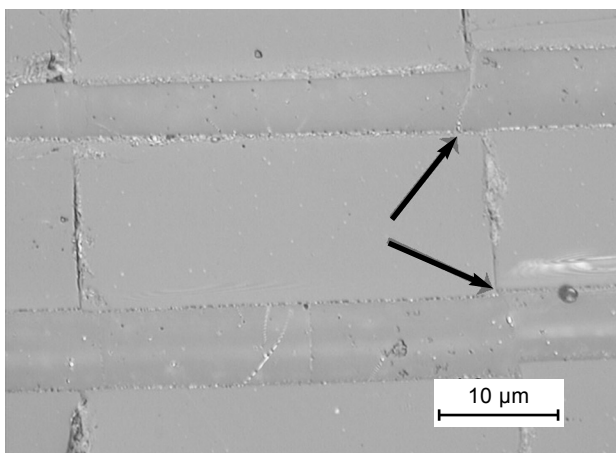


Figure 4. Cracked fibres (arrows) in the composite A pyrolysed at 700°C.

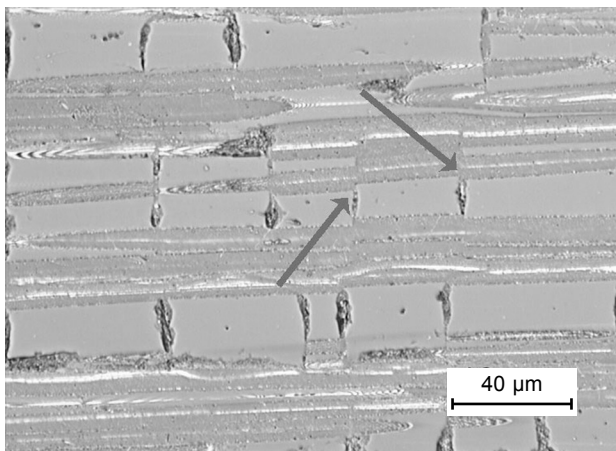


Figure 5. Cracked fibres (arrows) in the composite A pyrolysed at 700°C.

Methods

Microstructure of the composites was investigated by light microscopy of their cross-sections mounted in a transparent resin and polished by diamond paste. A Nikon Optiphot-100 microscope equipped with the Hitachi HV-C20 TV camera and a digital image grabbing system were used.

The oxidation procedure of the specimens consisted in heating them in nitrogen environment to the target temperature at a rate of 50 K/h, shutting the feed of nitrogen and introducing the dried air at a flow rate of 1 l/min at a constant temperature (700 or 800°C). After the chosen oxidation period the oxidation was finished by restoring the feed of nitrogen and cooling at a rate of 70 K/h.

The Young's modulus was measured in a four-point flexural arrangement at a 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 made by Maytec, Germany) was employed. The sample deflection measurement using a high-temperature extensometer with resolution 0.1 µm was described in detail earlier [10]. 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 speed 0.2 mm/min, and temperatures RT - 650°C. At least 5 repeated measurements were executed at each temperature.

The resonance frequency method was described in detail previously [11-12]. A specimen is suspended in carbon fibre loops reaching into the hot zone of the furnace. Vibrations are excited in the sample via a piezoelectric transducer and one of the carbon-fibre loops. The second piezoelectric transducer detects via another carbon-fibre loop the resonant vibrations of the sample. For the signal excitation and detection, a network analyser is used. Evaluation is performed by numerically solving Timoshenko's equation for vibrating beams and fitting the theoretical resonance frequencies to the experimental ones.

RESULTS AND DISCUSSION

Development of mechanical properties during pyrolysis

Initial stages of pyrolysis of the polysiloxane matrix were explored by monitoring the gradual development of Young's modulus and fracture surfaces of the unidirectional composites A treated to 400-700°C. The

temperature dependences of static Young's moduli measured in a four-point flexural arrangement (Figure 6) reveal that the increasing pyrolysis temperature has but a minor effect on the room-temperature modulus and that a substantial decrease of modulus occurs above 600°C.

Three-point flexural loading of these composites to failure at the temperature of their pyrolysis yielded fracture with participation of dissipative processes, which decayed gradually towards higher pyrolysis temperatures (400 to 600°C) and simultaneously the material became more brittle. At 650°C, however, the plastic deformation occurred above a certain load level.

There is no much difference in the appearance of the fracture surfaces generated at different temperatures. An interesting development can be seen, however, in the surfaces generated by cleavage along fibres (using a razor) where a tendency towards a more consolidated material emerges with increasing temperature of pyrolysis (Figure 7 a-c).

Oxidation - induced mass loss and microstructural changes

In order to establish the proneness to oxidation, the specimens B and C (pyrolysed to 800°C and once densified) were exposed to hot air at gradually increased temperature and time and the mass loss was determined. Figure 8 shows that at the oxidation temperature of 700°C the mass loss is significantly higher for the L901-based composite than for the M130-derived one. Further oxidation steps at the same or even elevated temperatures lead to much less mass loss but, as a rule, the L901-derived matrix loses more mass than the M130-derived one (Figure 8). The microstructural change is visible in the optical microscope images in Figure 9. For the matrix L901 (Figure 9b), a lot of matrix cracking is observed and the fibres are less

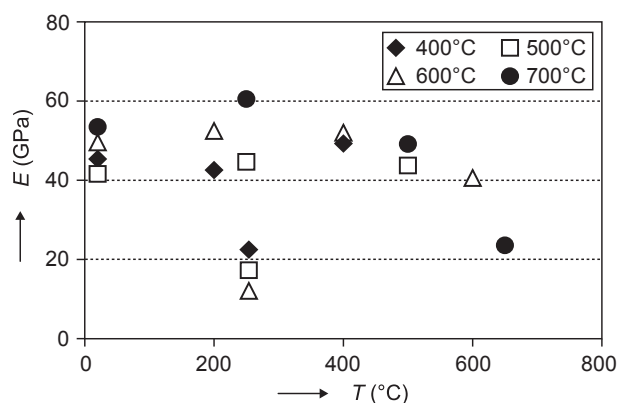
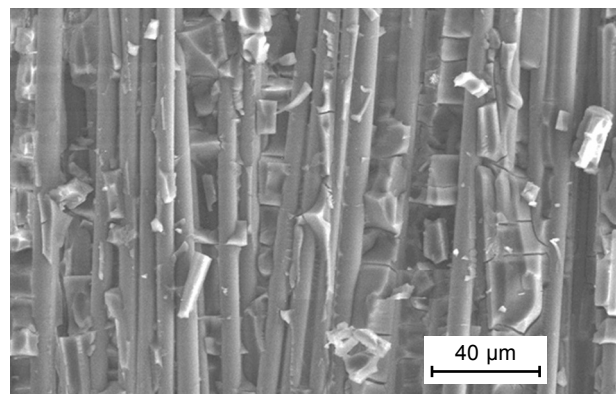


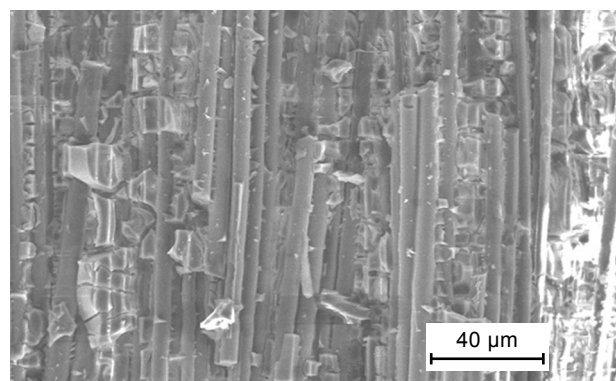
Figure 6. Temperature dependence of the flexural Young's modulus of unidirectional composites A (basalt fibres + M130) pyrolysed to 400, 500, 600, or 700°C.

deformed, whereas for M130 (Figure 9a) the adhesion of fibre and matrix seems to be very strong and the fibre deformation is much more distinct. This effect is even more pronounced for longer oxidation times (Figure 9 c, d).

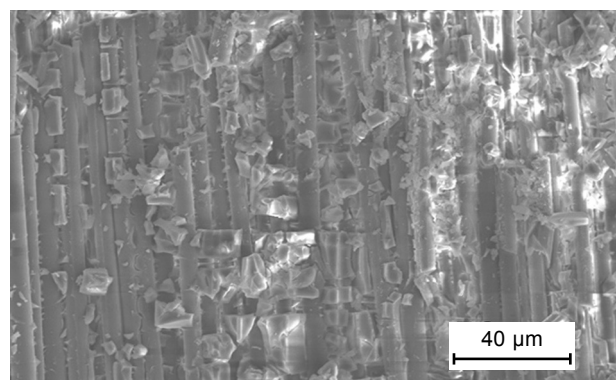
The higher aspect ratio (ratio of larger to smaller diameters of the fibres from image analysis of 50 fibres) shows quantitatively the higher deformation of the basalt fibres in the material with the matrix M130 (Figure 10).



a)



b)



c)

Figure 7. Cleavage surface of the composite A (basalt fibres + M130) pyrolysed to: a) 400°C, b) 500°C, c) 600°C.

Microstructure and elastic properties after intensive oxidation

The heavy oxidation damage of the L901-based composites (Figure 8) is probably due to a larger proneness to oxidation of the pyrolysis residua of phenyl groups if compared to that of methyl ones [13]. Our attention hereafter focused to another matrix precursor:

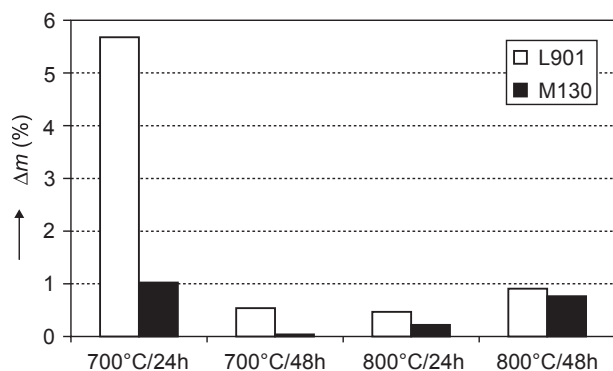
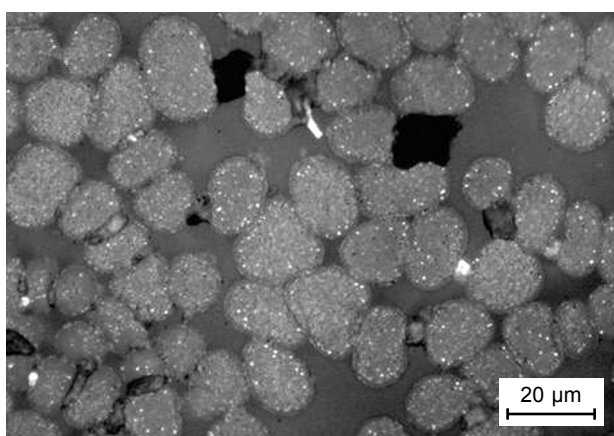
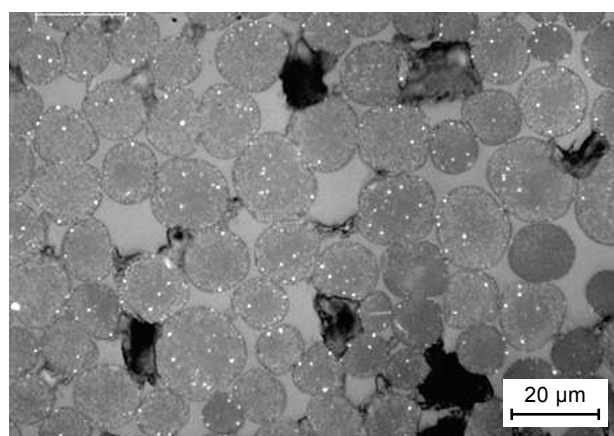


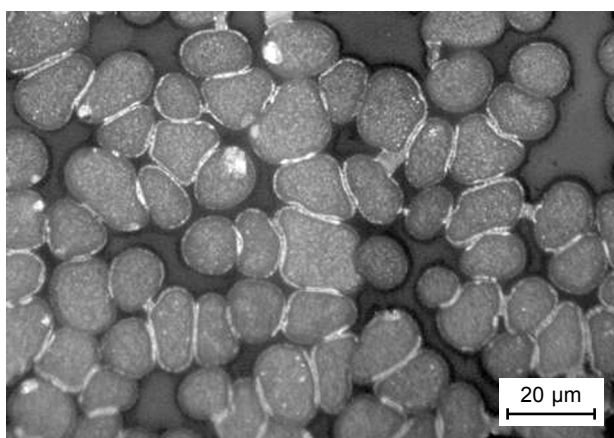
Figure 8. Weight loss of the composites B and C with matrix derived from L901 and M130 during successive oxidation steps in air.



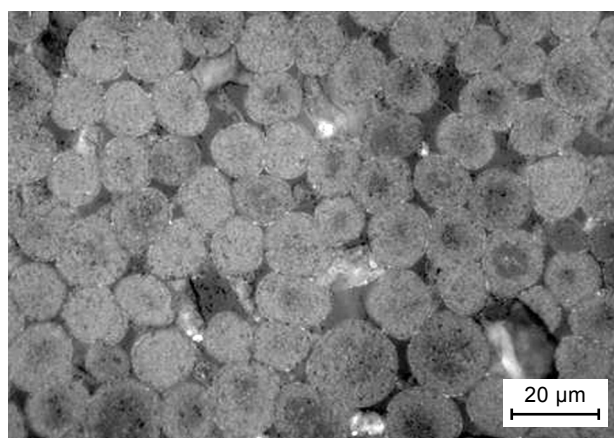
a)



b)



c)



d)

Figure 9. Optical microscopy image of the unoxidised composite: a) C with the M130-derived matrix, b) B with the L901-derived matrix, c) C with the M130-derived matrix oxidised for 72 h at 700°C, d) B with the L901-derived matrix oxidised for 72 h at 700°C.

the M130 polymethylsiloxane resin. The corresponding specimens D were made by pyrolysing the precursing polymer composites with the M130 at a rate 10 K/h between 300 and 700°C and - after 1 h soaking at this temperature - by controlled cooling at the same rate 10 K/h. The careful manufacture process resulted in a more homogeneous microstructure of the initial material (Figure 11a, 11b).

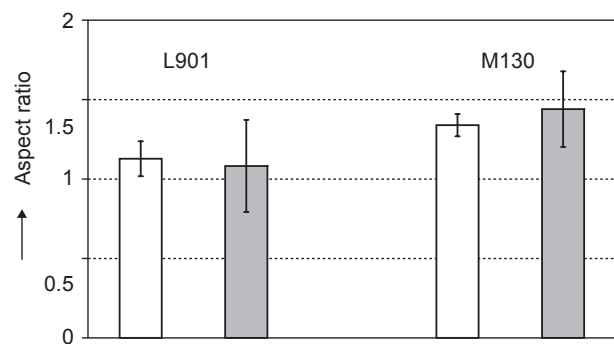


Figure 10. Aspect ratio (larger to smaller diameter) of the fibres in the composites B and C before and after oxidation for 72 h at 700°C (light bars - unoxidised, dashed bars - oxidised). Mean values and error bars are plotted.

The anisotropic elastic moduli E (Young's) and G (shear) were measured in air using the resonant beam technique. For each of both (mutually perpendicular) directions of flexural vibration with respect to the layered structure of the specimens one set of Young's and shear moduli was obtained. If the specimens exhibit no gradient the "in-plane" and "out-of-plane" Young's moduli are identical but the shear moduli are different due to the anisotropy of the layered composite.

In Figure 12a and 12b, temperature dependence of the in-plane moduli of the unoxidised specimens D are plotted (the out-of-plane shear modulus behaves similarly). The measurement was performed in two runs up to 700°C and down to RT. The Young's modulus (Figure 12a) adhered to the same path (within experimental error margins) proving thus a thermal stability of the material. The Young's modulus, however, decreases with increasing measurement temperature.

Compared to the Young's modulus, the shear modulus (Figure 12b) diminished in the 1st run above 500°C and kept decreasing even in the initial stage of cooling.

In the 2nd run, however, only negligible variations of G were observed, which suggest that the shear modulus got (almost) stabilized.

Generally, the shear modulus of composites with polysiloxane-derived matrix increases remarkably with the treatment temperature [14], which corresponds to the gradual reconstruction of the originally polymer matrix to a pre-ceramic one. In our case, however, the tested material had already passed the manufacturing process and the polymer reconstruction should be completed. The observed decrease of the shear modulus is probably connected with the appearance of micro-cracks.

After the measurement of the initial elastic behaviour of the composite D (Figure 12a, 12b), the same specimens were exposed to hot air (700°C) for an extended period in order to simulate the anticipated operating conditions of the composite. The oxidation process was performed in 2 steps with duration 24 and 120 h. The mass loss after the entire oxidation process was 0.2 % which confirms the excellent material stability in the harsh environment.

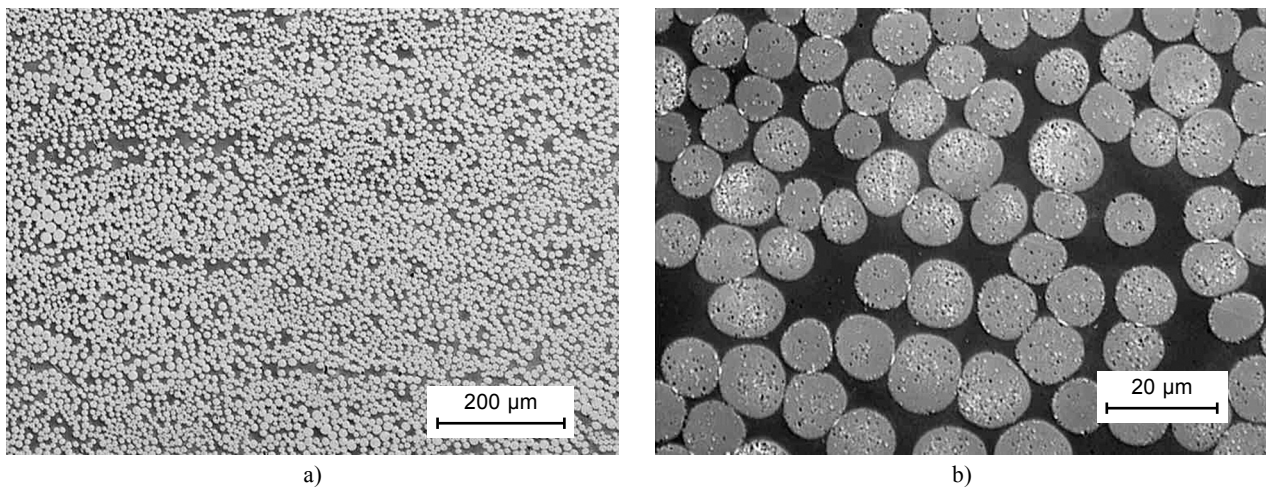


Figure 11. Optical microscopy images from the unoxidised composite D with the M130-derived matrix.

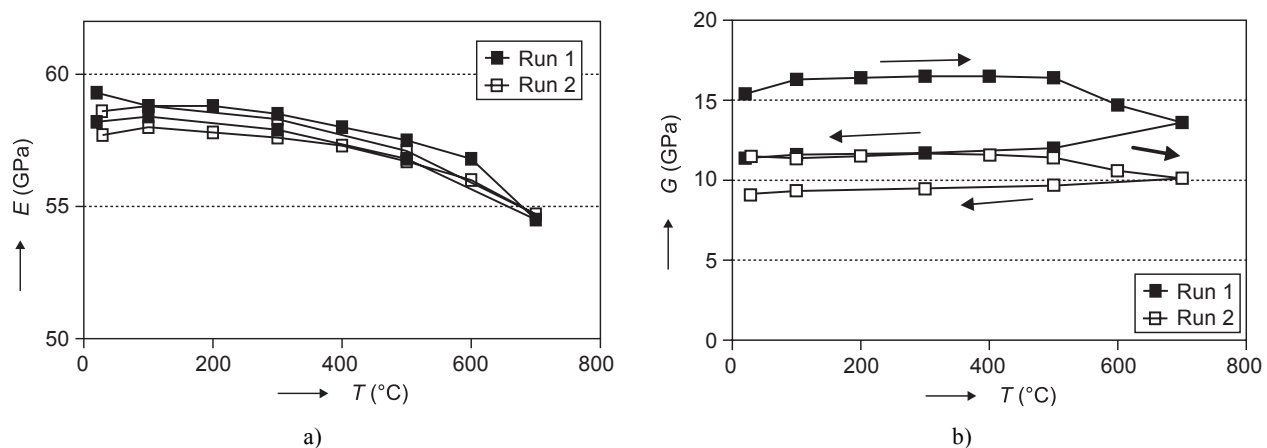


Figure 12. Temperature dependence of the modulus E (a) and the in-plane shear modulus G (b) in the 1st and 2nd heating/cooling run of the unoxidised composite D.

Nevertheless, after 48 h of oxidation at 700°C the microstructure revealed some matrix cracking (Figure 13a, 13b). After 120 h of oxidation at 700°C numerous

matrix cracks and fibre/matrix gaps emerge (Figure 14a, 14b), together with a pronounced plastic deformation of the fibres (Figure 14b).

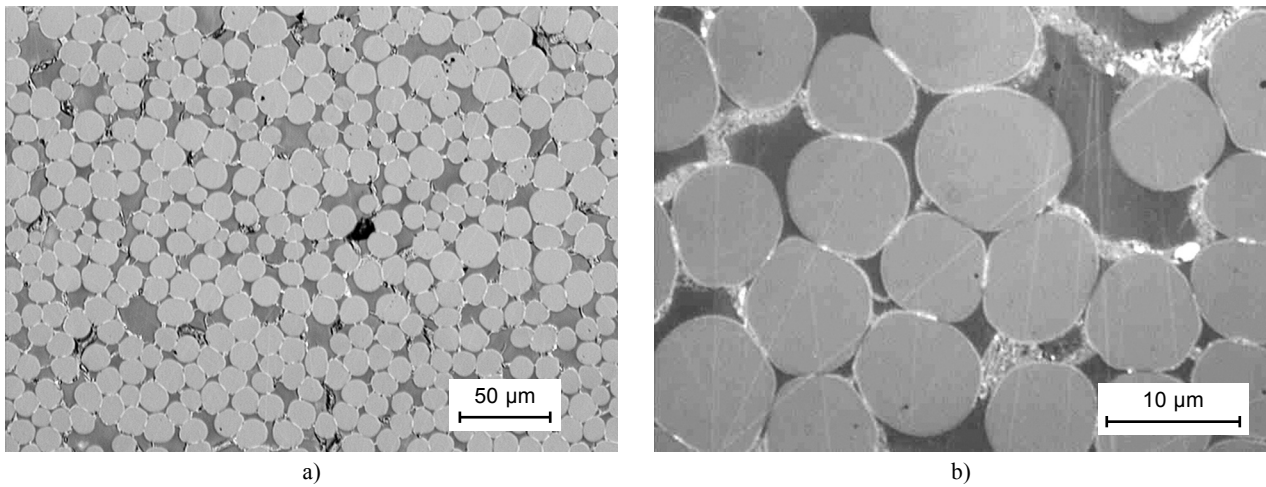


Figure 13. Optical microscopy images of the composite D with the M130-derived matrix oxidised 48 h at 700°C.

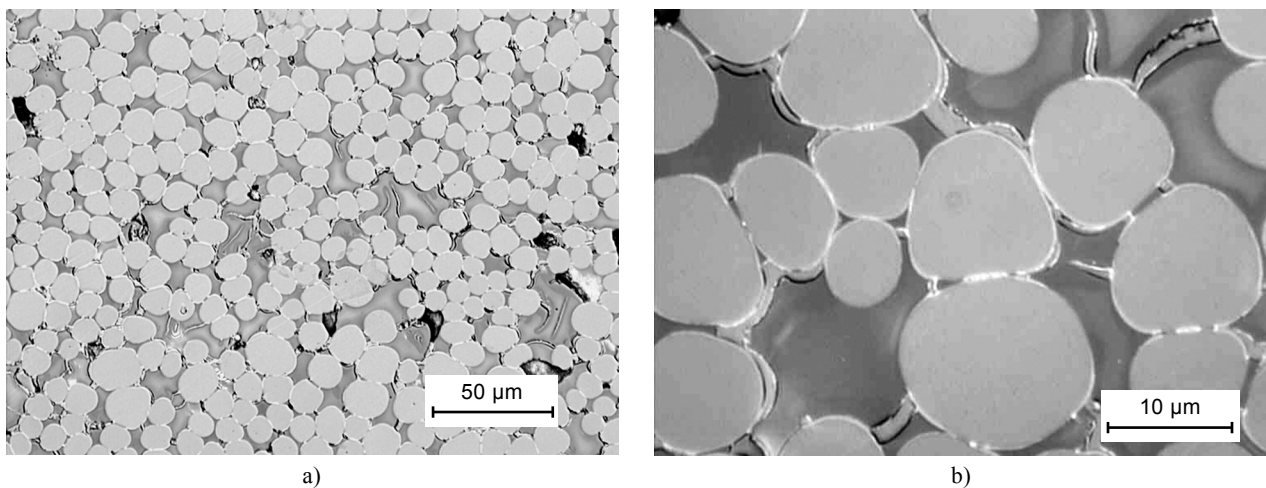


Figure 14. Optical microscopy images of the composite D with the M130-derived matrix oxidised 120 h at 700°C.

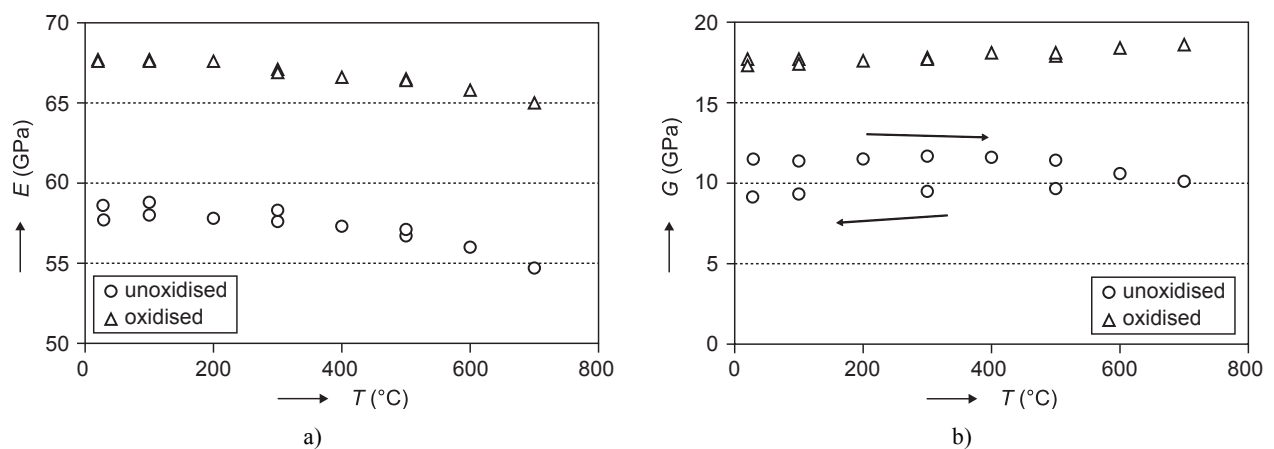


Figure 15. Temperature dependence of the a) in-plane modulus E and b) in-plane shear modulus G : the 2nd heating/cooling run of the unoxidised and oxidised (144 h at 700°C) composite D.

Despite the microstructure damage, the elastic and shear moduli significantly improved after the oxidation. Figures 15a, 15b compare the in-plane elastic and shear moduli in the 2nd heating/cooling run prior to oxidation with the measurement after oxidation (the out-of plane moduli behave similarly).

The increase of both E and G moduli after the oxidative heat treatment should be attributed to the profound structural changes of the polymer matrix which gradually transforms to a ceramic matter. The increase of the matrix moduli prevails in its implications over the deteriorating effect of matrix cracking (Figure 14a, 14b). Elucidation of the role of oxygen in the observed variations of the moduli and distinguishing between the effects of pure heat treatment and environment chemistry will require further study.

The governing role of matrix in forming the shear modulus of the composite is even more clearly revealed in the angular dependence of G in the fabric reinforced composite [15]. In specimens cut along principal directions of the rectangular reinforcement pattern the in-plane shear modulus is predominantly controlled by the matrix as the fabric contributes weakly to the shear stiffness. In a parallel study the composite specimens E reinforced with a basalt fabric (plain weave, weft and warp linear density 100 tex, area density 270 g/m²) and the matrix derived from the M130 polysiloxane resin were processed in the same way as the unidirectional composites D investigated in the present study. The influence of the oxidation processing on the in-plane shear modulus of the fabric reinforced composites E is plotted in Figure 16. The numerical value for the in-plane shear modulus increases almost by a factor of two for specimens with oxidation processing, consistently for unidirectionally and fabric reinforced composites.

CONCLUSION

Composites manufactured by pyrolysis of the M130 polymethylsiloxane resin reinforced with continuous basalt fibres (Sudovodskoye Steklovolokno) reveal remarkable thermal stability in air up to 700-800°C. Both tensile and shear moduli of the composite increase after exposition to hot air though con-

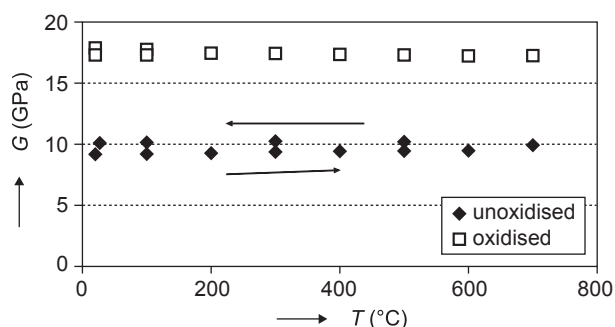


Figure 16. Temperature dependence of the in-plane shear modulus G of the fabric reinforced composite E : the 2nd heating/cooling run of the unoxidised and oxidised (144 h at 700°C) composite.

siderable matrix cracking takes place during this treatment. This finding testifies for a predominance of the processes connected with the transformation of the polymer matrix into a ceramic one over those due to the defective matrix structure.

Acknowledgement

The presented investigation was supported by the Austrian - Czech Kontakt project No. WTZ 2004-17 and by the Institute's research plan AVOZ30460519.

References

1. Sim J., Park C., Moon D.Y.: Compos. Pt. B-Eng. 36, 504 (2005).
2. Park J.M., Shin W.G., Yoon D.J.: Compos.Sci.Technol. 59, 355 (1999).
3. Matko S., Anna P., Marosi G., Szep A., Keszei S., Czigany T., Posloskei K.: Macromol.Symp. 202, 255 (2003).
4. Czigany T.: Mater.Sci.Forum 59 473-474, (2005).
5. Bashtannik P.I., Ovcharenko V.G., Boot Y.A.: Mech.Compos.Mater. 33, 600 (1997).
6. Ozturk S.: J.Mater.Sci. 40, 4585 (2005).
7. Artemenko S.E.: Fibre Chem. 35, 226 (2003).
8. Černý M., Glogar P., Sucharda Z., Machovič V.: Ceramics - Silikáty 49, 145 (2005).
9. Černý M., Glogar P., Goliáš V., Hruška J., Jakeš P., Sucharda Z., Vávrová I.: Ceramics-Silikáty 51, 82 (2007).
10. Černý M., Glogar P.: J.Mater.Sci. 39, 2239 (2004).
11. Lins W., Kaendl G., Peterlik H., Kromp K.: Rev.Sci.Instr. 70, 3052 (1999).
12. Loidl D., Puchegger S., Kromp K., Zeschky J., Greil P., Bourgeon M., Peterlik H.: Adv.Eng.Mater. 6, 134 (2004).
13. Brus J., Kolář F., Machovič V. and Svítlová J.: J. Non-Cryst. Solids 289, 62 (2001).
14. Černý M., Glogar P., Hron P., Sucharda Z., Machovič V., Bednářová D. and Hytychová S.: In: Proceedings of ECCM-11 Conference, Rhodes, May, 2004 (CD, section Ceramic Matrix Composites) 2004.
15. Černý M., Glogar P., Manocha L.M.: Carbon 38, 2139 (2000).

MIKROSTRUKTURA A MECHANICKÉ VLASTNOSTI TEPELNĚ ODOLNÝCH KOMPOZITŮ VYZTUŽENÝCH ČEDIČOVÝMI VLÁKNY

PETR GLOGAR, ZBYNĚK SUCHARDA, MARTIN ČERNÝ,
STEPHAN PUCHEGGER*, HERWIG PETERLIK*

Ústav struktury a mechaniky hornin, v.v.i. AVČR
V Holešovičkách 41, 18209 Praha 8
Institut für Materialphysik, Universität Wien,
Boltzmannngasse 5, A-1090 Wien, Österreich

Byly studovány mechanické vlastnosti, mikrostruktura a odolnost vůči oxidaci jednosměrných kompozitů vyrobených z komerčně dostupných polysiloxanových pryskyřic vyztužených nekonečnými čedičovými vlákny. Po pyrolýze výchozích kompozitů při 600-800°C byla polymerní matrice postupně přetvořena na keramickou, charakterizovanou jen malou hmotnostní ztrátou při oxidaci v horkém vzduchu. Po dlouhodobé expozici ve vzduchu při 700 nebo 800°C vznikly četné trhliny matrice a došlo k plastické deformaci vláken, i přes poškození mikrostruktury se ale podstatně zlepšil elastický a smykový modul. Toto zlepšení může být způsobeno změnami struktury polymerní matrice při její transformaci na keramický materiál, které ve svých důsledcích převáží nad negativními vlivy trhlín.