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MECHANICAL BEHAVIOR OF POLYSILOXANE MATRIX – BASED COMPOSITE REINFORCED WITH BASALT FIBRES AT ELEVATED TEMPERATURES

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ABSTRACT
The study focused to unidirectionally reinforced basalt fibre composites with a matrix derived by partial pyrolysis at 650 – 750 °C from commercially available polysiloxane precursors. Mechanical properties of the basalt fibres Basaltex and Kamenny Vek were studied. The creep which occurs above 600 °C is a limiting factor for their utilization at elevated temperatures. Above 750 °C their mechanical properties deteriorate due to commencing crystallization which also hampers their suitability as reinforcement in composites designated for elevated temperatures. The composite pyrolysed at 650 °C revealed the best room – temperature properties. Its exploitation in a common environment up to 550 °C is possible but some reduction of strength and fracture toughness must be taken in consideration which takes place already after its short-time exposition in hot air.

KEYWORDS: composite material, mechanical properties, basalt fibres

1. INTRODUCTION

New structural materials are investigated for applications under hostile conditions at elevated temperatures and in an aggressive (oxidative, acid, alkaline) environment. Among them, composites reinforced with thermally stable fibres (e.g., R-glass fibres or fine ceramic fibres based on silicon carbide or oxides like alumina) are perhaps the most promising. The merit of expensive fibrous reinforcement consists in improving the toughness and strength of naturally brittle ceramic matrix, which itself, however, can be obtained by a relatively cheap polymer - pyrolysis route from polymer precursors like polysiloxane resins or others. Utilization of cheap basalt fibres in combination with commercially available resins therefore offers a unique potential for developing inexpensive composite materials with remarkable performance at temperatures limited by the thermal stability of basalt. The properties and behaviour of various composites with continuous or short basalt fibres have been studied recently by many authors. The basalt fibres were investigated as reinforcement in composites with a concrete (Sim et al., 2005) or a polymer matrix: epoxy (Park et al., 1999), polypropylene (Matko et al., 2003; Czigány, 2005; Bashtannik et al., 1997) or phenol-formaldehyde resin (Ozturk, 2005; Artemenko, 2003). Fibre-matrix interface properties were studied in various basalt fibre - polymer matrix systems, e.g. in (Sim et al., 2005), (Park et al., 1999) and (Jančář, 2006).

Our targets were

a) to explore and master laboratory-scale manufacture process of composites reinforced with basalt fabric or yarn with matrix derived by pyrolysis of polysiloxane resins,
b) to study mechanical and thermo mechanical properties of the composites,
c) to investigate the impact of processing parameters on these properties and to optimise the process,
d) to pursue the degradation of composites after a prolonged exposition to hot air.

2. METHODS

2.1. PROPERTIES OF FIBRES

Tensile behaviour of fibre tows at elevated temperatures was measured at gauge length 25 mm using a universal testing machine INSPEKT 50 kN (made by Hegewald-Peschke, Germany) equipped with a high-temperature extensometer PMA-12/V7-1 (Fig. 1) with resolution 1 μm (made by Maytec, Germany). The sample deflection measurement using a high-temperature extensometer with resolution 0.1 μm was described in detail elsewhere (Černý and Glogar, 2004). Fig. 2 presents the scheme of the tensile measurement. A special attention had to be paid to the tow "conditioning" prior to tensile loading, i.e., smoothing particular filaments so that as many of them as possible would get under tension during the tow loading. The procedure was especially crucial before measuring the modulus.

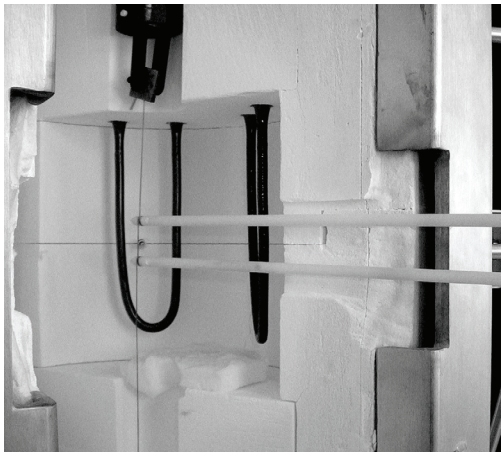


Fig. 1 View of alumina rods transducing the tow elongation to the extensometer through a slot in insulation of the furnace (now open).

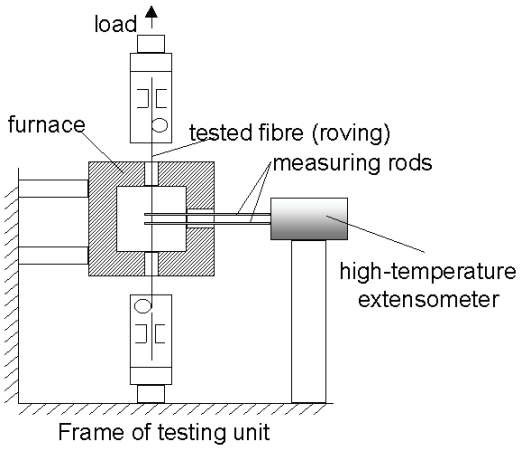


Fig. 2 Scheme of the tensile measurement of elasticity and creep on fibres at elevated temperature.

In order to guarantee a standard tensile load during tensile measurements, actual cross-sections of the fibre tows were determined from microscopic observation of the metallographically polished specimens with filaments mounted perpendicularly to the polished surface. The microscope Nikon Optiphot-100 equipped with an Image Analysis system Lucia was used for measurement of filament diameters.

2.2. PROPERTIES OF POLYMERS

Thermogravimetric analysis of the resins was performed using a Netzsch STA 409 apparatus at heating rate 10 °C.min^{-1} to 1200 °C. Approximately 50 mg specimens were placed in a platinum crucible; the flow of argon was adjusted to 75 ml.min^{-1}.

2.3. PREPARATION AND PROCESSING OF COMPOSITES

Unidirectional composites were made by the wet-winding (prepreg) route described in (Černý et al., 2005). Eight prepreg layers (length 160 mm, width 6 mm) were stacked in a heated mould, cured gradually for 6 hrs at 160 – 250 °C under uniaxial pressure of 0.6 MPa. The received polymer-matrix composites (specimen size approximately 45 × 4 × 1.5 mm^3) were further pyrolysed in nitrogen atmosphere (mostly to 650 or 750 °C but other pyrolysis temperatures between RT and 1000 °C were chosen occasionally).

During pyrolysis the polymer matrix was gradually transformed into an inorganic matrix (similar to silicon oxycarbide glass), which was accompanied by release of volatiles, mass loss, and void formation.

In order to assess their thermal stability some specimens were (prior to measuring their properties) exposed to hot air, i.e., oxidised. 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.

2.4. PROPERTIES OF COMPOSITES

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 Young's modulus was measured in a four-point flexural arrangement at a thickness to span ratio (1.5 – 2.0) / 40 at RT. A testing machine INSPEKT (made by Hegewald-Peschke, Germany) with a 5 kN load cell was employed. The flexural modulus E was calculated from the slope of the quasilinear part of the load-deflection curve. The room-temperature tests were performed at low loads (less than 15 N) and crosshead speed 0.2 mm/min.

The flexural strength was determined with the same apparatus in a three-point arrangement.

Room temperature elastic and shear properties of the composites were studied with help of the resonant frequency tester Erudite (CNS Electronics Ltd., London, UK) up to 100 kHz. The Young's modulus E was determined from the basic longitudinal resonant frequency of beams with free ends, and the in-plane shear modulus G was obtained from flexural vibrations by a resonant frequency method (Černý and Glogar, 1998).

Table 1 List of the investigated fibres.

	Grade	Producer	Type of product
BT1		Basaltex (http-1)	CBF
BT2		Kamennyj Vek (http-2)	CBF
GS1	RC 10	S. Gobain Vetrotex (http-3)	R-glass
GS2	RO 99	S. Gobain Vetrotex (http-3)	E-glass

Table 2 Cross-sections of filaments and tows.

	Average filament cross-section (μm^2)	Average number of filaments in a tow	Total tow cross-section (mm^2)
BT1	131.3 ± 61.5	1095 ± 8	0.143
BT2	129.6 ± 29.3	974 ± 5	0.126
GS1	89.9 ± 16.6	3980 ± 17	0.358
GS2	145.5 ± 35.8	770 ± 3	0.111

In contrary to other specimens, those exposed additionally to hot air broke during the flexural test in a brittle manner enabling thus to study their fracture surfaces by scanning electron microscopy (SEM) using the JEOL JSM-5410 apparatus. For this purpose, the fractured specimens were provided with an Au-Pd coating in order to increase their surface conductivity.

The fracture toughness was determined by Z. Chlup (Institute of Physics of Materials ASCR, Brno) in order to monitor the behaviour of the composites at various levels of pyrolysis: cured only (250 °C) and partially pyrolysed to 650 °C or 750 °C. According to the standard (ČSN), the chevron-notch specimens were loaded in a 3-point arrangement (strain rate 0.1 mm/min) at room temperature and at 550 °C. The measurement aimed at identification of failure micromechanisms and fracture characteristics of the investigated composites.

3. RESULTS

3.1. FIBRES

First, tensile behaviour at elevated temperatures of two commercially available basalt fibre types (BT1, BT2) were examined and their properties were compared to those of conventional glass fibres (GS1, GS2) (Table 1).

Cross-sections of the fibre tows as determined by image analysis are given in Table 2.

Behaviour of the tows loaded by a tensile stress 10 MPa and heated at a rate 15 K/min is plotted in Figure 3. All fibres start to shrink slightly above 400 °C, which is probably due to some plastic recovery originating in the manufacture process of the glassy material. On the other hand, the onset temperature of unlimited elongation (creep) differs for particular fibres. It equals approximately 580, 640, 840, and 700 °C for the fibres B1, B2, G1, and G2, respectively.

The endurance of the investigated CBF under tensile load at elevated temperatures is less than that of standard glass fibres. It may be caused by a higher content of alkali oxides in the used purely natural raw material. Militký (Militký et al., 2002) suggested that the CBF fracture probably occurs due to nonhomogeneities in fiber volume, probably near the small crystallites of minerals.

Tensile modulus of the tows BT1, BT2, GS1, and GS2 was measured under low load at temperatures up to 600 °C. Repeated mountings of the tows yielded slightly different values of modulus, ranging 70 – 80 GPa. Their temperature dependences, however, were very similar. For the sake of clarity, values of modulus E_T at temperature T were normalized to the room-temperat\ure value E_{RT} and their ratio was plotted in the graph (Fig. 4). Uncertainty of the plotted mean values is less than ± 0.02.

The GS1 fibres retain their modulus completely up to 450 °C and lose but 8 % of its RT value at 600 °C. The fibres GS2 and BT2 are mutually similar: they lose 3 – 4 % of the RT modulus at 400°C and 8 - 10 % at 450 °C. At 500 °C the BT2 seems to slightly outperform the GS2 (loss 12% for BT2

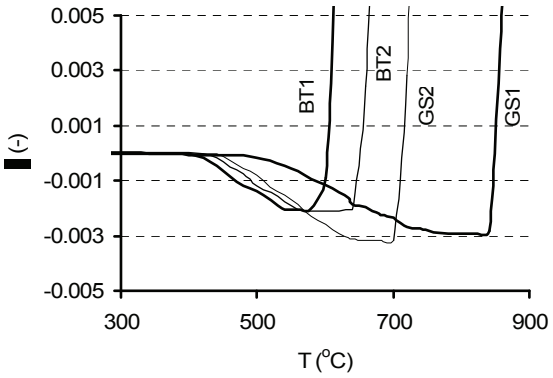


Fig. 3 Elongation of the fibre tows BT and GS under constant tensile load at increasing temperature.

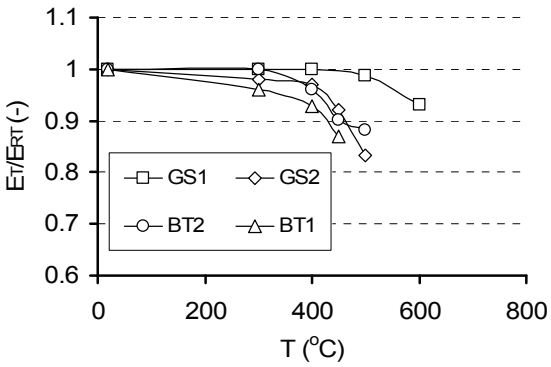


Fig. 4 Temperature dependence of the normalized tensile modulus of the fibres BT1, BT2, GS1 and S2.

Table 3 Properties of the investigated matrices before and after pyrolysis to 1000 °C.

Product	Type	before pyrolysis		after pyrolysis		mass residue after pyrolysis (%)	volume shrinkage after pyrolysis (%)
		density ($g.cm^{-3}$)	Young's modulus (GPa)	density ($g.cm^{-3}$)	Young's modulus (GPa)		
Lukosil M130	polymethylsiloxane resin	1.22	2.3	2.02	80	87	47
Lukosil L901	polymethylphenyl siloxane resin	1.19	2.6	1.95	80	82	50

compared to 17% for GS2). The fibre BT1 exhibits a drop of 13 % already at 450°C. The overall pattern of the E (T) dependence corresponds to the established in Figure 3 superiority of the fibre GS1 over the GS2, BT2 and BT1 fibres in tensile properties at elevated temperatures.

3.2. MATRICES

Polysiloxane resins L901 (polymethyl-phenylsiloxane) or M130 (polymethylsiloxane) made by Lučební závody, Czech Republic, were used as matrix precursors. The process of their pyrolysis in nitrogen was characterized by the changes of density and Young's modulus, and by values of the mass residue and volume shrinkage after pyrolysis (Table 3).

Total pyrolytic transformation of the polysiloxane resins - i. e. the transformation of an organic into an inorganic material - takes place around 1000 °C. Their partial pyrolysis at lower temperatures leads to formation of intermediate states between polymer and refractory silicon oxycarbide.

3.3. COMPOSITES

Two types of commercially available continuous basalt fibre tows and two types of polysiloxane resins supplied by the Lučební závody Kolín (Czech Republic) were employed as matrix precursors. By combining these precursors and fibres four composite batches were produced (Table 4).

The composites were processed in a way described in 2.3.

Mechanical properties of the primary (unoxidised) specimens measured at RT are strongly influenced by the final pyrolysis temperature. For a special series of composites treated to 250, 420, 650, 750, or 1000 °C the shear modulus (Fig. 5) is minimum for the pyrolysis temperature 420 °C which corresponds to the elsewhere established poor integrity of the polysiloxane treated to 350 – 450 °C (Balík et al., 2003) and it reaches its maximum for 750 °C. The Young's modulus, on the other hand, steadily increases with increasing pyrolysis temperature up to 750 °C (Fig. 6).

The composites pyrolysed to 650 °C reveal maximum flexural strength exceeding that of the

Table 4 Labelling of the investigated composite types.

Fibre	Resin	Composite	Fibre	Resin	Composite
Basaltex	L901	B1	Kamenny Vek	L901	KV1
	M130	B2		M130	KV2

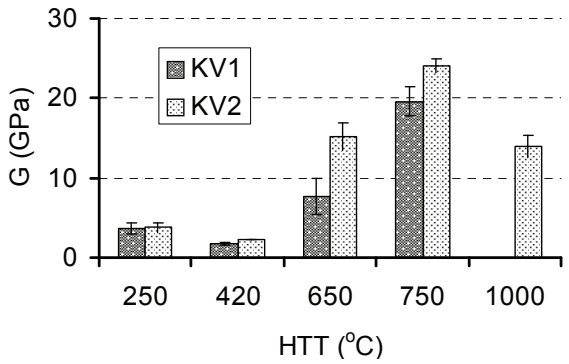


Fig. 5 Shear modulus measured by resonant frequencies of composites treated to 250, 420, 650, 750, and 1000 °C.

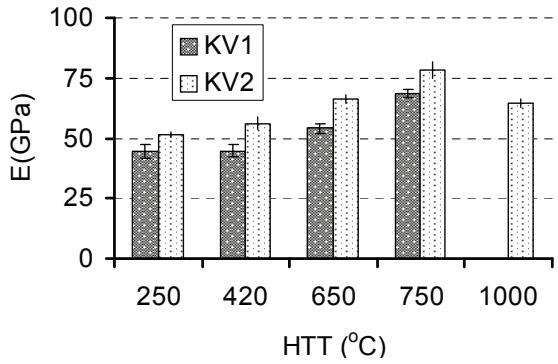


Fig. 6 Young's modulus measured by resonant frequencies of composites treated to 250, 420, 650, 750, and 1000 °C.

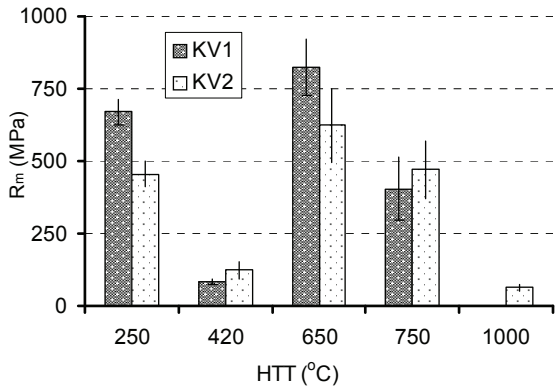


Fig. 7 Flexural strength of composites KV1 and KV2 treated to 250, 420, 650, 750, and 1000 °C.

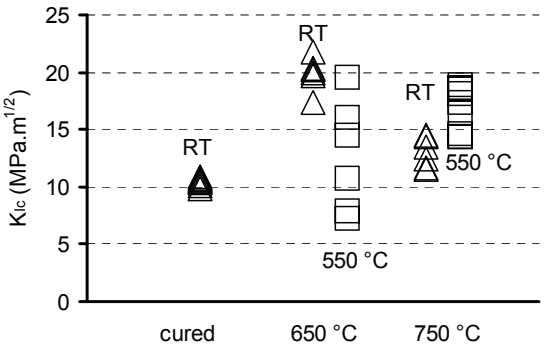
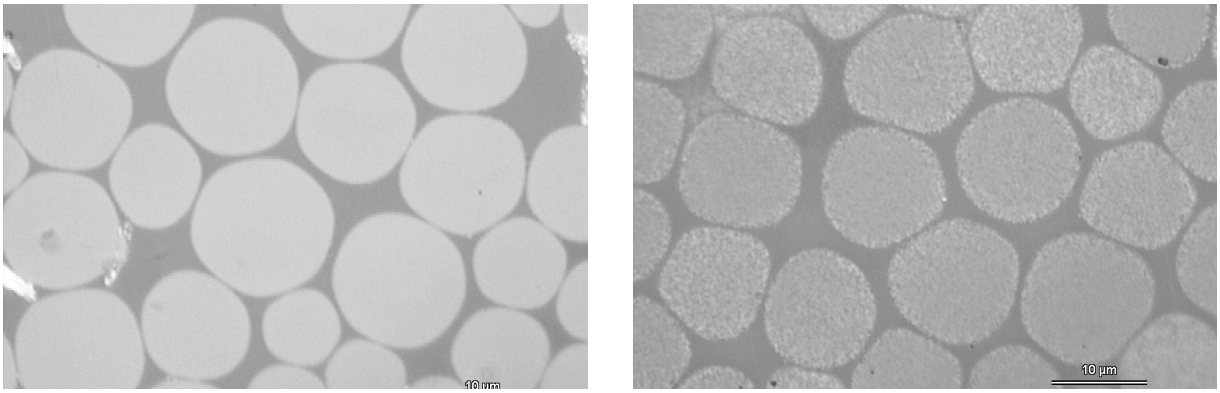


Fig. 8 Fracture toughness of the composites KV2 either cured or pyrolysed to 650 °C or 750 °C measured at room temperature - △ or 550 °C - □.

cured material (Fig. 7). At higher pyrolysis temperatures, however, the flexural strength declines and it is extremely low after heat treatment to 1000 °C, which is probably due to the onset of structural changes of the reinforcing basalt fibres. Similarly to the shear modulus (Fig. 5) the partial pyrolysis to 420 °C leads to very low flexural strength (Fig. 7).

Fracture toughness was determined for the composites KV2 in various states of thermal treatment: cured or pyrolysed to 650 °C or 750 °C. At room temperature the K_{Ic} of the composites pyrolysed to 650 °C reached maximum values 17.3 – 21.8 MPa.m$^{1/2}$ (Fig. 8). Accordingly, these composites will be at low temperatures more resistant to fracture damage than those only cured or pyrolysed to 750 °C. At 550 °C, however, the fracture toughness of the composites pyrolysed to 750 °C prevails (Fig. 8).

Optical micro photographs of the composite with the B1 fibre and polymer-derived matrix heat treated to 650 °C and 750 °C are in Fig. 9a and Fig. 9b. Due to matrix shrinkage during the thermal treatment the shape of (originally circular) fibre cross-sections is plastically distorted. A distinct difference between the fibre appearances is seen: after the treatment to 750 °C the fibre cross-sections are finely granular while they are completely plain at 650 °C. This



9a 9b

Fig. 9 Optical micro photographs of the cross-sections of the unidirectional composite with the basalt fibres heat treated to 650 °C (Fig. 9a) and 750 °C (Fig. 9b).

peculiarity can be attributed to the mentioned above (4.1) onset of fibre recrystallization.

3.4. MECHANICAL PROPERTIES OF COMPOSITES AFTER EXPOSITION TO HOT AIR

It was desirable to trace the development of mechanical properties of the studied composites over a wide period of the oxidation heat treatment. For this purpose, a large series of the KV1 and KV2 specimens was subjected to intermittent treatment in air at 550 °C with breaks at 1, 66, 90, 115, 140, 161, and 240 h. At each break two specimens were removed from the furnace and their flexural strength and Young's modulus were measured. The average values for the specimen pairs are plotted in Figure 10.

It can be stated that even oxidation at 550 °C deteriorates the flexural strength to levels 50 – 90 MPa. After approximately 10 h there seems to be but very weak dependence on the heat treatment duration (Fig. 10) and the fracture is brittle in all cases.

The Young's modulus retains values 50 – 75 GPa, which are also almost independent of the heat treatment duration.

3.5. APPEARANCE OF THE FRACTURE SURFACES

A detailed inspection (Glogar et al., 2007) of the fracture surfaces generated in flexural strength tests revealed small to moderate vertical articulation where ridges separate mutually inclined plateaus with no or small numbers of protruding fibres. Fibre pull-out (the basic toughening mechanism for fibrous composites) is present only occasionally in the specimens pyrolysed to 650 °C (Fig. 11, Fig. 12) and is totally absent in those pyrolysed to 750 °C (Fig. 13).

Much more often, the propagating crack cuts the fibres before than they can break farther from the crack plane. It explains the brittle fracture and the mostly catastrophic pattern of the load-displacement characteristic of the flexural test. As a consequence, the specimen behaves more or less like a monolith and

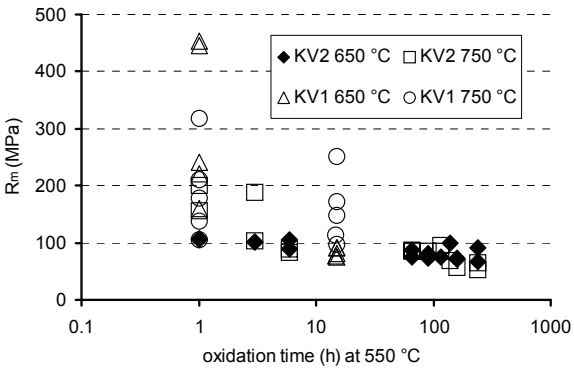


Fig. 10 Flexural strength after exposition to air at 550 °C in dependence on the oxidation duration.

does not fully utilize the potential of the reinforcing fibres.

The reason for the absence of pull-out can be sought in excessively strong bonding of the fibres to the matrix. Even some coalescence between adjacent fibres is not excluded at 750 °C, especially in the case of insufficient resin penetration into the tow (Fig. 14). These unfavourable fracture features of the oxidized specimens should be remedied by some appropriate surface treatment of the fibres.

Appearance of the chevron-notch specimens after flexural fracture is demonstrated by Fig. 15. The extent of fibre pull-out and its character varied slightly in dependence on the temperatures of the test and of the pyrolysis. In Fig. 15, the fracture surface revealed a distinct and homogeneously distributed pull-out of individual fibres (not bundles) with a considerable length. In this case the fracture toughness reached K_{Ic} = 14.5 MPa.m$^{1/2}$. Under other conditions the pull-out contributed less to the energy-dissipating mechanisms; nevertheless in some cases the fracture toughness was even higher due to matrix fragmentation and higher effectiveness of fibre-matrix friction.

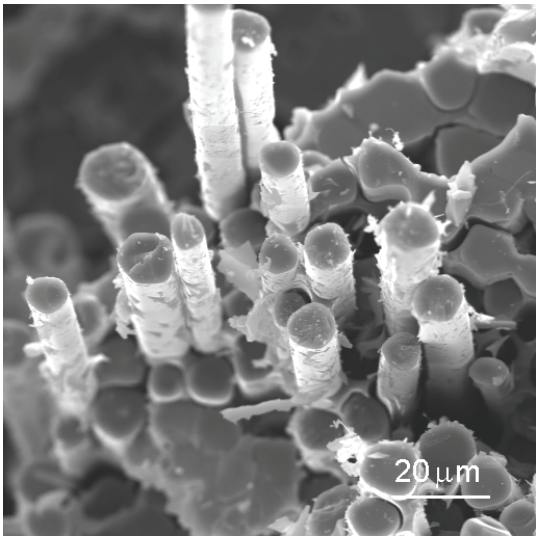


Fig. 11 Fibre pull-out in the fractured B2 composite pyrolysed and oxidised at 650 °C.

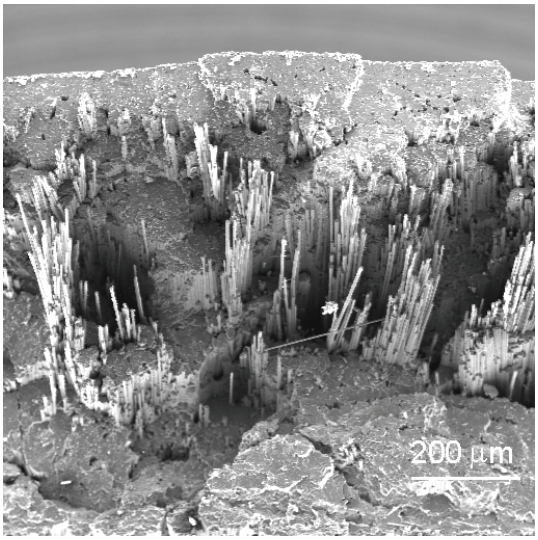


Fig. 12 Fibre pull-out in the fractured B2 composite pyrolysed and oxidised at 650 °C.

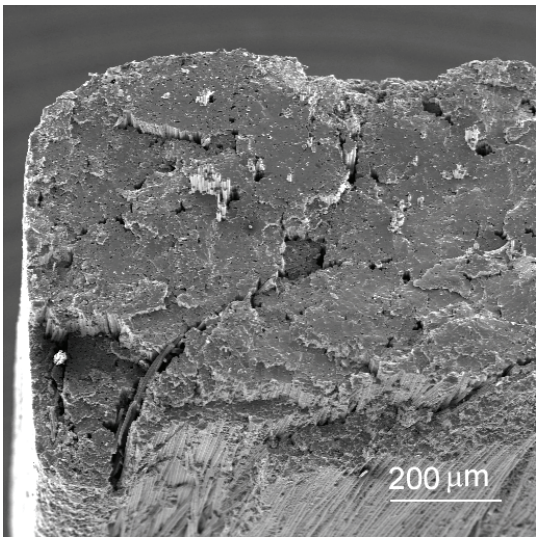


Fig. 13 Fracture surface of the B2 composite pyrolysed and oxidised at 750 °C.

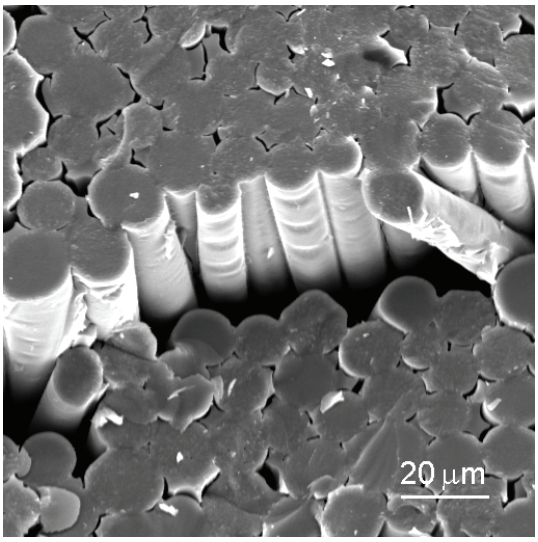


Fig. 14 Fibre coalescence in the fractured B1 composite pyrolysed and oxidised at 750 °C.

CONCLUSIONS

Mechanical properties of commercially available basalt fibres Basaltex and Kamenny Vek were investigated. Mechanical tests demonstrate that the creep which occurs significantly above 580 °C (Basaltex) or 640 °C (Kamenny Vek) is a limiting factor for their utilization at elevated temperatures. Above 750 °C their mechanical properties deteriorate due to commencing crystallization which also hampers their suitability as reinforcement in composites destined for elevated temperatures. The study focused on unidirectionally reinforced composites with a matrix derived from polysiloxane precursors by partial pyrolysis at 650 – 750 °C. The composite pyrolysed at 650 ° C revealed the best room – temperature properties. Its exploitation in a common environment up to 550 °C is possible but some reduction of strength and fracture toughness must be taken in consideration which takes place already after its short-time exposition in hot air.

ACKNOWLEDGEMENT

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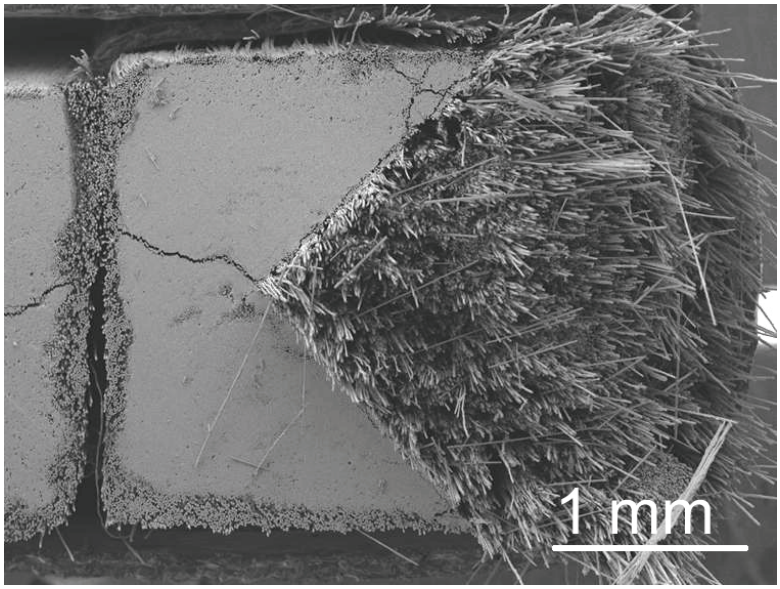

Fig. 15 Chevron-notched specimen of the composite KV2 pyrolysed to 750 °C after a fracture toughness test at room temperature.

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