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COMPOSITE MATERIALS WITH BASALT FIBRE REINFORCEMENT AND PYROLYSED POLYSILOXANE MATRIX

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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 and chemical 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. On the basis of these results the technology of preparation of basalt fibre composites was developed. 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 being sought 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.

2. PROJECT OBJECTIVES

The project objectives were

a) to explore laboratory-scale manufacture process of composites reinforced with basalt 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,

e) to employ basalt fibres from the domestic production made of microwave heated raw material and to optimise their properties.

3. METHODS

The three investigators were determined to contribute to the project according their specialisation. Technical University of Liberec (TUL) intended to study mechanical, surface and chemical properties of basalt fibres and dynamic mechanical properties of composite specimens up to 800 °C. MDI Technologies (MDI) planned to use their own laboratory unit with microwave melting for manufacturing continuous basalt fibre from domestic sources. Unfortunately, P. Jakeš died already in 2005 and the fibre production in MDI was virtually cancelled. In this report only the methods used and results achieved by the 1st joint investigator (IRSM) and his subcontractor are presented.

Table 1 List of the investigated fibres.

	Grade	Producer	Type of product
BT1		Basaltex (http1)	CBF
BT2		Kamenny Vek (http2)	CBF
GS1	RC 10	S. Gobain Vetrotex (http3)	R-glass
GS2	RO 99	S. Gobain Vetrotex (http3)	E-glass

3.1. PROPERTIES OF FIBRES

Tensile behaviour of fibre tows at elevated temperatures was measured using a universal testing machine INSPEKT 50 kN (made by Hegewald-Peschke, Germany) equipped with a high-temperature extensometer PMA-12/V7-1 (made by Maytec, Germany).

The X-ray diffraction (XRD) was used to detect structural changes, which may occur due to thermal treatment of the investigated fibres. The measurements were carried out by V. Goliáš at the Institute of Geochemistry, Mineralogy and Mineral resources, Faculty of Science, Charles University, Prague (Černý et al., 2007).

3.2. PREPARATION AND PROCESSING OF COMPOSITES

Unidirectional composites were made by the wet-winding (prepreg) route described in (Černý et al., 2005). 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).

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

3.3. PROPERTIES OF COMPOSITES

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 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 (Černý and Glogar, 1998).

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.

4. RESULTS

4.1. FIBRES

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) – see Table 1.

Behaviour of the tows loaded by a tensile stress 10 MPa and heated at a rate 15 K/min is plotted in Fig. 1. 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.

Tensile modulus of the tows BT1, BT2, GS1, and GS2 was measured under low load at temperatures up to 600 °C. For the sake of clarity, values of modulus E_T at temperature T were normalized to the room-temperature value E_{RT} and their ratio was plotted in the graph (Fig. 2). Uncertainty of the plotted mean values is less than ± 0.02.

The overall pattern of the E (T) dependence corresponds to the established in Fig. 1 superiority of the fibre GS1 over the GS2, BT2 and BT1 fibres in tensile properties at elevated temperatures.

By treating the investigated fibres above 650 °C some structural changes emerged which were detected by the X-ray diffraction (Černý et al., 2007). The basalt fibres BT1 and BT2 heat treated to 750 °C revealed in their XRD patterns sharp diffraction maxima, which thus manifested presence of crystalline phases. These phases in the BT1 fibre were identified as clinopyroxene and spinel. In the BT2 fibre only a spinel phase was identified. The amount of crystalline phases in the studied basalt fibres is very low, probably below 1 wt.%.

4.2. MATRICES

Polysiloxane resins L901 (polymethylphenylsiloxane) or M130 (polymethylsiloxane) made by Lučební závody, Czech Republic, were used as matrix precursors (Table 2).

4.3. COMPOSITES

Two types of commercially available continuous basalt fibre tows and two types of polysiloxane resins

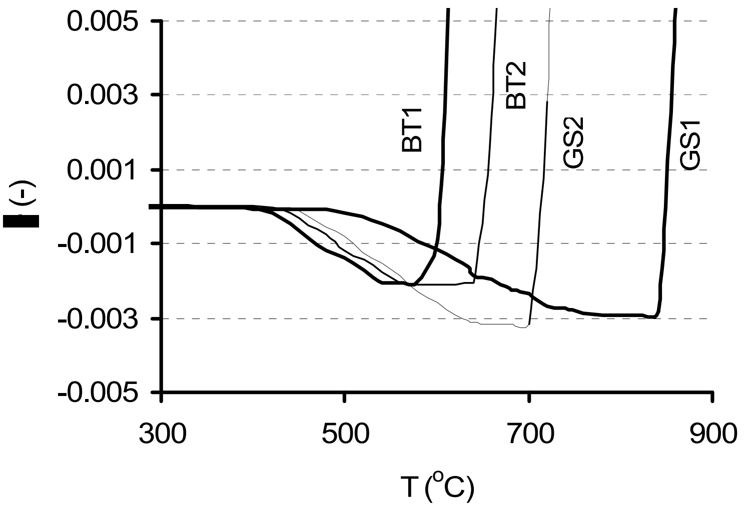

Fig. 1 Elongation of the fibre tows BT and GS under constant tensile load at increasing temperature.

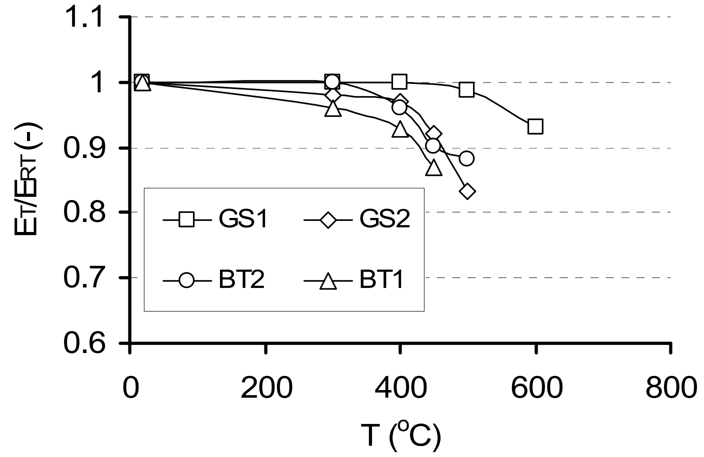

Fig. 2 Temperature dependence of the normalized tensile modulus of the fibres BT1, BT2, GS1 and S2.

Table 2 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

Table 2 Labelling of the investigated composite types.

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

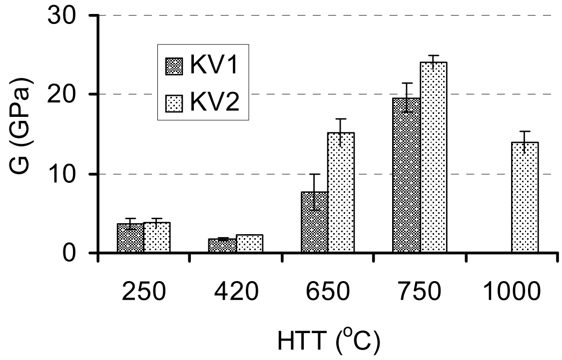

Fig. 3 Shear modulus measured by resonant frequencies of composites treated to 250, 420, 650, 750 and 1000 °C.

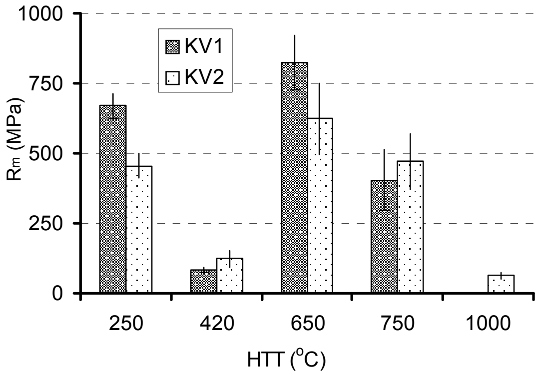

Fig. 4 Flexural strength of composites KV1 and KV2 treated to 250, 420, 650, 750 and 1000 °C.

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 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. 3) is minimum for the pyrolysis temperature 420 °C 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.

The composites pyrolysed to 650 °C reveal maximum flexural strength exceeding that of the cured material (Fig. 4). 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. 3) the partial pyrolysis to 420 °C leads to very low flexural strength (Fig. 4).

4.4. MECHANICAL PROPERTIES OF COMPOSITES AFTER EXPOSITION TO HOT AIR

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 was measured. Even the oxidation at 550 °C deteriorates the flexural strength to similar levels (50 – 90 MPa) like those observed after treatment to higher temperatures. After approximately 10 h there seems to be but very weak dependence on the heat treatment duration and the fracture is brittle in all cases.

4.5. 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 is present only occasionally in the specimens pyrolysed to 650 °C (Fig. 5, Fig. 6) and it is totally absent in those pyrolysed to 750 °C.

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. The reason for the absence of pull-out can be sought in excessively strong bonding of the fibres to the matrix.

5. CONCLUSIONS

Mechanical and chemical properties of commercially available basalt fibres Basaltex and Kamenny Vek were investigated. Mechanical tests demonstrate that the creep which occurs significantly

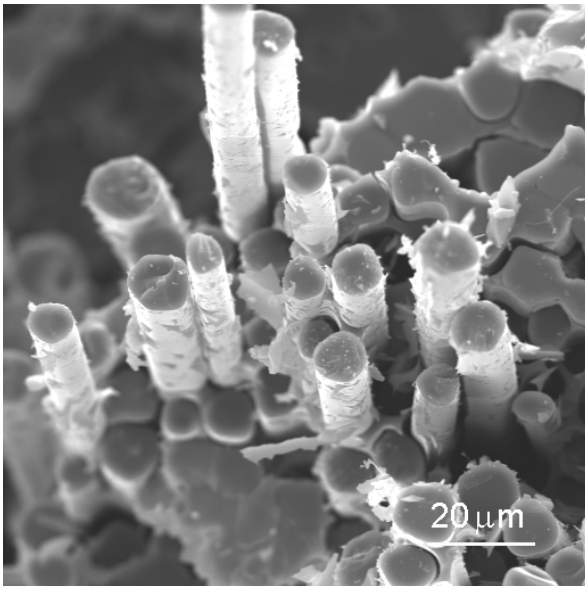

Fig. 5 Fibre pull-out in the fractured B2 composite pyrolysed and oxidised at 650 °C.

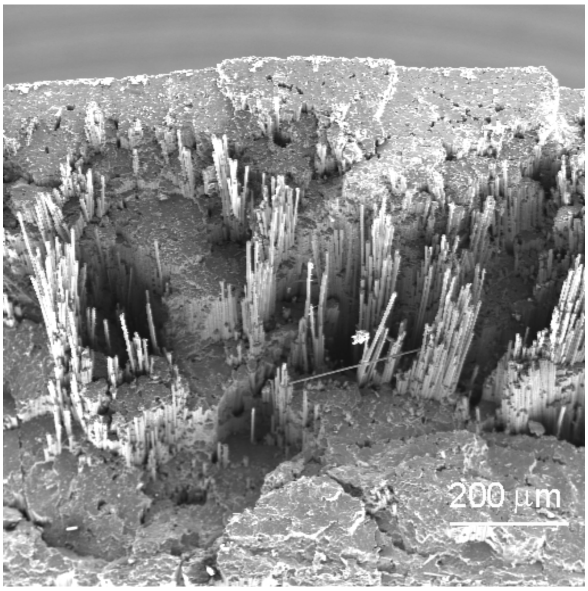

Fig. 6 Fibre pull-out in the fractured B2 composite pyrolysed and oxidised at 650 °C.

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 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.

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http3 – http://www.vetrotextextiles.com/pdf/E_R_and_D_glass_properties.pdf

KOMPOZITNÍ MATERIÁLY VYZTUŽENÉ ČEDIČOVÝMI VLÁKNY S PYROLYZOVANOU POLYSILOXANOVOU MATRICÍ

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ABSTRAKT:
Projekt byl zaměřen na studium jednosměrně vyztužených vláknových kompozitů s čedičovými vlákny a matricí odvozenou částečnou pyrolýzou při 650 – 750 °C z komerčně dostupných polysiloxanů. Byly studovány mechanické a chemické vlastnosti čedičových vláken zn. Basaltex a Kamenny Vek. Nad 600 °C se projevoval creep, omezující jejich použitelnost při zvýšených teplotách. Nad 750 °C se mechanické vlastnosti zhoršily kvůli nastupující krystalizaci. Na základě výsledků studia čedičových vláken byla vyvinuta technologie přípravy kompozitů s čedičovými vlákny. Nejlepší mechanické vlastnosti při laboratorní teplotě má kompozit pyrolyzovaný v dusíku při 650 °C. Lze předpokládat jeho použití v běžném prostředí do 550 °C, je však třeba počítat s jistým omezením pevnosti a lomové houževnatosti, k nimž dochází i po krátké expozici v horkém vzduchu.