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FRACTURE BEHAVIOUR OF THE BASALT FIBRE REINFORCED COMPOSITES WITH POLYSILOXANE-DERIVED MATRIX

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ABSTRACT
Selected mechanical properties of unidirectional composites with polysiloxane-derived matrix and continuous basalt fibres reinforcement are presented. A special attention is devoted to the impact of long term exposition in hot air (aimed as a simulation of the anticipated operating conditions) to the composite failure under flexural load. The investigated composites worsened their properties after treatment in air at elevated temperature (650 – 750 °C). The originally non-catastrophic flexural failure changed to a brittle fracture, which was accompanied with a flexural strength decrease. The coalescence of fibres and their strong interaction with the matrix are probably the main reasons for the onset of brittleness. Unless these drawbacks are resolved the service temperature of the composites in air will probably not exceed approximately 500 °C.

KEYWORDS: basalt fibre, composite, fracture behaviour, polysiloxane, precursor

INTRODUCTION

Fibre reinforced composites find their utilization in the rapidly broadening field of applications. Some composite types can be considered as structural materials for usage at elevated temperatures. Ideally they should be lightweight, chemically and thermally stable, possessing good mechanical properties and cheap. Actually, no real material reveals these properties altogether.

Recently, attention has been devoted to continuous basalt fibres (CBF) whose primary advantage (according to http://www.basaltex.com/) consists in their low cost, good resistance to acids and solvents, and good thermal stability (under very low stress up to 1250 °C, under common load only to 500 °C). They were investigated as reinforcement in composites with concrete (Sim et al., 2005) or polymer - epoxy (Park et al., 1999), polypropylene (Matko et al., 2003), (Czigány, 2005), (Bashtannik et al., 1997) or phenol-formaldehyde resin (Ozturk, 2005), (Artemenko, 2003) matrix. Fibre – matrix interface properties were studied in various basalt fibre – polymer matrix systems in, e.g., (Park et al., 1999) or (Matko et al., 2003).

Good thermal stability of CBF allows even utilizing their reinforcing function in fibrous composites manufactured by means of an additional heat treatment, e.g., pyrolysis (up to 750 °C in nitrogen) of a polymer matrix composite, which yields a ceramic matrix composite. For this purpose, selected polysiloxane resins are suitable as matrix precursors (Černý et al., 2005).

Mechanical properties of CBF at elevated temperatures have been investigated in (Černý et al., 2007). Here, a significant loss of tensile modulus above 400 °C was established. When loaded in tension by 10 MPa and heated, an unlimited elongation of the CBF tow commenced at 580 – 640 °C (depending on the fibre type). This fibre behaviour can play a certain role in forming the microstructure of the pyrolysed CBF - reinforced composites, because the latter are subjected to varying temperature and stress fields during manufacture. In this way, mechanical properties of the pyrolysed composites can be affected by parameters of the manufacturing process.

In this paper selected mechanical properties of unidirectional composites with polysiloxane-derived matrix and CBF reinforcement are presented. A special attention is devoted to the impact of long term exposition in hot air (aimed as a simulation of the anticipated operating conditions) to the composite failure under flexural load.

MATERIALS

Two types of commercially available continuous basalt fibre tows were utilized for composite manufacturing in laboratory: Basaltex and Kamennyj Vek. Their basic properties are summarized in Table 1. These fibres were exploited either in their original state or after removing the lubrication by extraction in toluene (because of the a-priori unknown behaviour of the lubricant after heat treatment). Two types of polysiloxane resins supplied by the Lučební

Table 1 Basic properties of the used basalt fibre tows.

	Producer	Average filament cross-section (μm^2)	Average number of filaments in a tow	Total tow cross-section (mm^2)	Linear density (10^{-6} kg.m^{-1})
B	Basaltex [http://www.basaltex.com/]	131.3 ± 61.5	1095 ± 8	0.143	374
KV	Kamennyj Vek [http://www.basfiber.com/en/roving.shtml]	129.6 ± 29.3	974 ± 5	0.126	344

Table 2 Labelling of the investigated composite types.

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

závody Kolín (Czech Republic) were employed as matrix precursors: polymethylsiloxane resin M130 and polymethylphenylsiloxane resin L901. Their behaviour when thermally cured and subsequently pyrolysed has been investigated recently (Černý et al., 2005). By combining two precursor types and two fibre types 4 composite batches were obtained (Table 2). Each batch broke down to 2 subtypes: with and without fibre lubrication.

Unidirectional composites were made by the wet-winding (prepreg) route described in (Černý et al., 2005). Eight prepreg layers were stacked in a heated mould, cured gradually for 6 h at 160 – 225 °C and post cured at 250 °C for 4 h under uniaxial pressure of 0.6 MPa. The received polymer-matrix composites (specimen size approximately $45 \times 4 \times 1.5$ mm^3) were further pyrolysed in nitrogen atmosphere to 650 or 750 °C. 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 (4 h at 650 or 750 °C).

METHODS

An electrodynamic resonant frequency tester Erudite (CNS Electronics Ltd., London, UK) was used for measurement of resonant frequencies of composite specimens up to 100 kHz. The tensile modulus E was then determined from the basic longitudinal resonant frequency of a beam with free ends, and the in-plane shear modulus G was obtained from flexural vibrations by a resonant frequency method (Černý and Glogar, 1998). For static measurements of the tensile modulus in a four-point flexural arrangement (thickness to span ratio (1.5 – 2.0) / 40) a testing machine Inspekt (made by Hegewald-Peschke, Germany) with a 5 kN load cell was used. The flexural strength was determined with the same apparatus in a three-point arrangement.

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.

RESULTS

MECHANICAL PROPERTIES

In Fig. 1 and Fig. 2 the results for E and G moduli from resonant frequency measurements are plotted. Removing the fibre lubrication deteriorated the elastic properties of the investigated materials which is most notable for the KV composites pyrolysed to 750 °C (Fig. 2). Minute interlaminar cracks emerging during pyrolysis are probably responsible for the shear modulus decline.

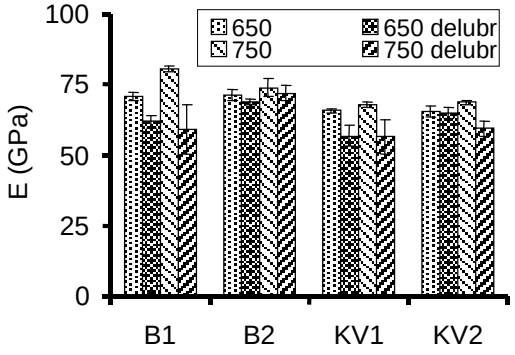

Fig. 1 Elastic modulus measured by resonant frequencies.

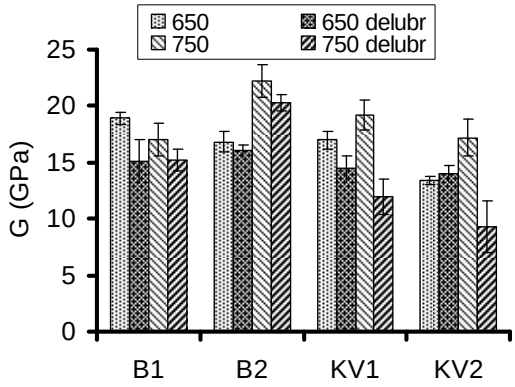

Fig. 2 Shear modulus measured by resonant frequencies.

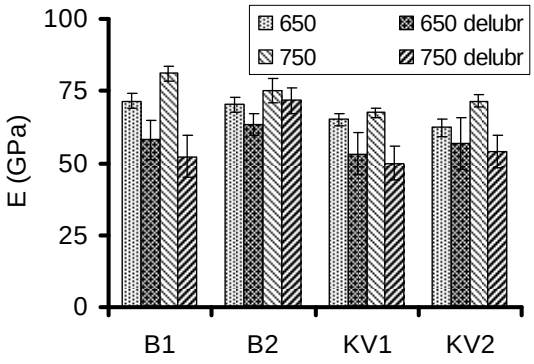

Fig. 3 Elastic modulus measured in a 4-point flexural arrangement.

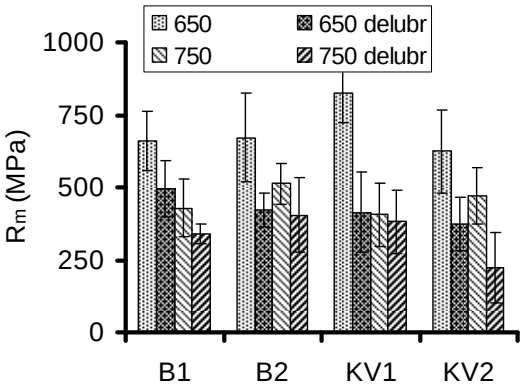

Fig. 4 Flexural strength measured in a 3-point flexural arrangement.

The static measurements yielded for the tensile modulus and flexural strength the data plotted in (Fig. 3) and (Fig. 4). During the flexural strength tests the specimens did not break in a brittle manner and they kept integrity even after failure (at large deformations).

The flexural strength is more sensitive to the treatment temperature (650 or 750 °C, Fig. 4) than the modulus (Fig. 3, Fig. 1). While slightly higher values of modulus (especially in case of lubricated fibres) were detected with the specimens treated to 750 °C, a distinct fall of strengths occurred for all specimens treated to this temperature instead of 650 °C. It follows that the composites should rather be pyrolysed to lower temperatures which, on the other hand, implies lowering their threshold operational temperature.

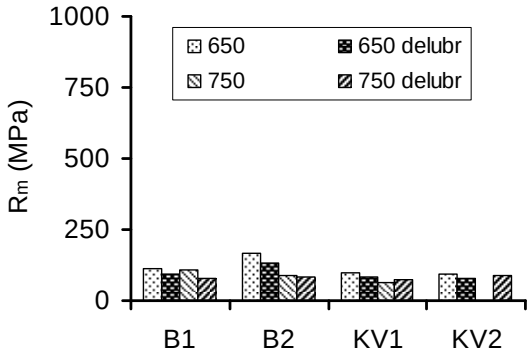

Fig. 5 Flexural strength after exposition to hot air.

EXPOSITION TO HOT AIR

Exposition to hot air ("oxidation", 4 h at 650 or 750 °C) deteriorated the flexural strength of the studied composites to 60 - 120 MPa (Fig. 5).

In all cases the fracture was brittle and the specimens broke cleanly to (at least) two parts. The fracture surfaces were investigated by scanning

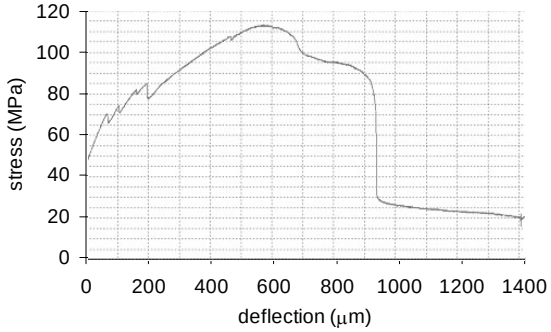

Fig. 6 Load – displacement curve of the specimen failed by delamination.

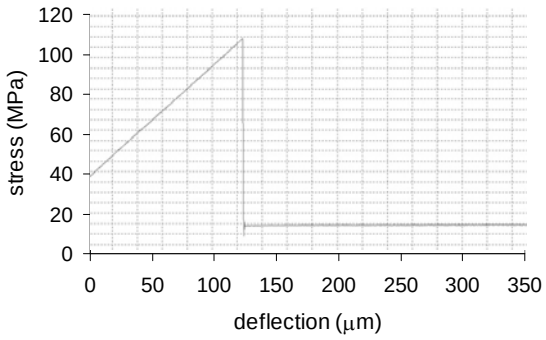

Fig. 7 Load – displacement curve of the specimen failed in a brittle manner.

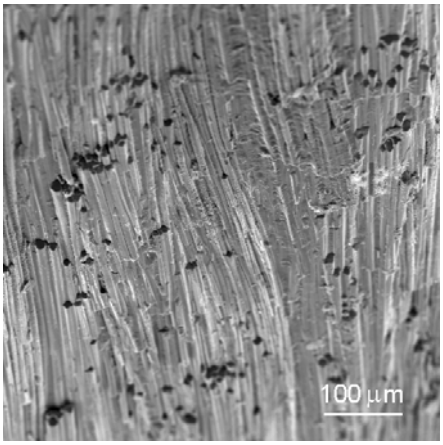

Fig. 8 Non-parallel fibres in the delamination plane. (B2 with lubricated fibres, pyrolysed and oxidised at 750 °C).

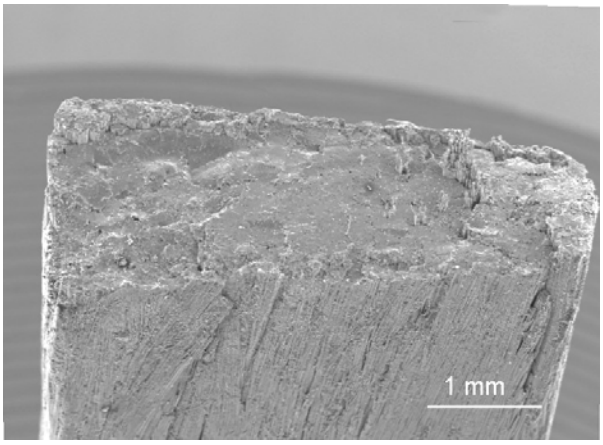

Fig. 9 Overall view at 40° tilt. (KV2 with delubricated fibres, pyrolysed and oxidised at 650 °C).

electron microscopy in a secondary electron mode emphasizing the surface topography.

ANALYSIS OF FRACTURE SURFACES

Total of 16 fracture surfaces were examined and many photographs ware taken, mostly at tilt 20° (perpendicular view or tilt 40° were used sporadically).

Only in two cases (the B2 composites with lubricated fibres oxidized to 650 and 750 °C) the specimens failed partly by *delamination* (Fig. 6). As both delaminated specimens originated from the same batch the reason for delamination could be sought in a defect lay-out of the involved prepreg. Indeed, in Fig. 8 a considerable level of fibre non-parallelism in the delamination plane can be seen. Non-ideally arranged fibres do not allow regular filling of inter-fibre gaps by the matrix and may cause an easier separation of the lamina.

Most of the investigated fracture surfaces, however, split the broken specimen into 2 parts and reveal small to moderate vertical articulation where ridges separate mutually inclined plateaus with no or small numbers of protruding fibres, Fig. 9. Fibre *pull-out* (the basic toughening mechanism for fibrous composites) is present only occasionally, namely in the B2 composite with lubrication (Fig. 10) as well as without lubrication (Fig. 11, Fig. 12).

Much more often the propagating crack cuts the fibres before than they can break farther from the crack plane (Fig. 13). It explains the *brittle fracture* and the mostly catastrophic pattern of the load-displacement characteristic of the flexural test (Fig. 7). As a consequence, the specimen behaves more or less like a monolith and does not fully utilize the potential of reinforcing fibres.

The reason for the absence of pull-out can be sought in a too strong bonding of fibres to matrix. Even some coalescence between adjacent fibres is not excluded at 750 °C, especially in case of insufficient resin penetration into the tow (Fig. 14, Fig. 15). These unfavourable fracture features of the oxidized specimens should be remedied by some appropriate surface treatment of the fibres.

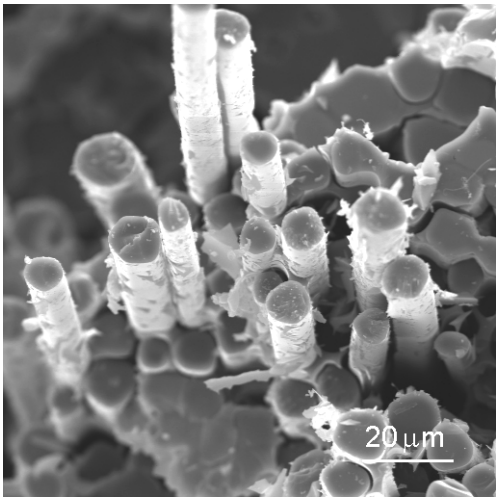

Fig. 10 Fibre pull-out (B2 with lubricated fibres, pyrolysed and oxidised at 650 °C).

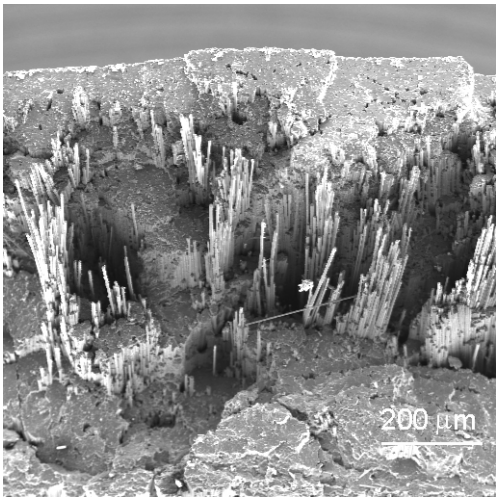

Fig. 11 Fibre pull-out (B2 with delubricated fibres, pyrolysed and oxidised at 650 °C).

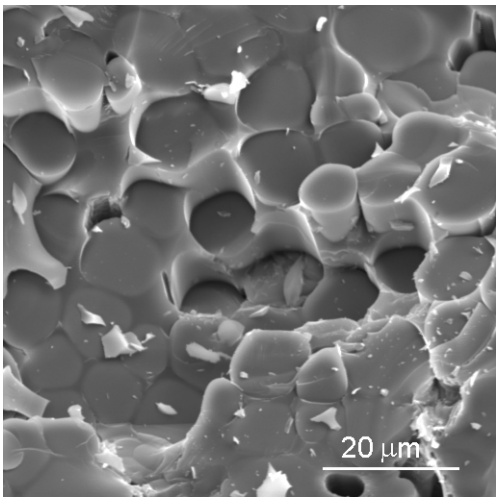

Fig. 12 Fibre pull-out (B2 with delubricated fibres, pyrolysed and oxidised at 650 °C).

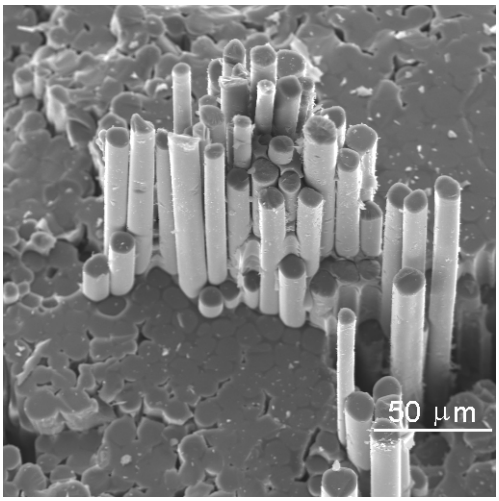

Fig. 13 Flat fracture plane (front, left) (B1 with delubricated fibres, pyrolysed and oxidised at 650 °C)

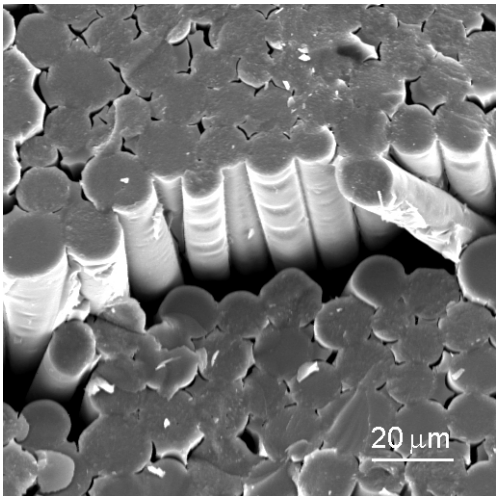

Fig. 14 Fibre coalescence (B1 with lubricated fibres, pyrolysed and oxidised at 750 °C).

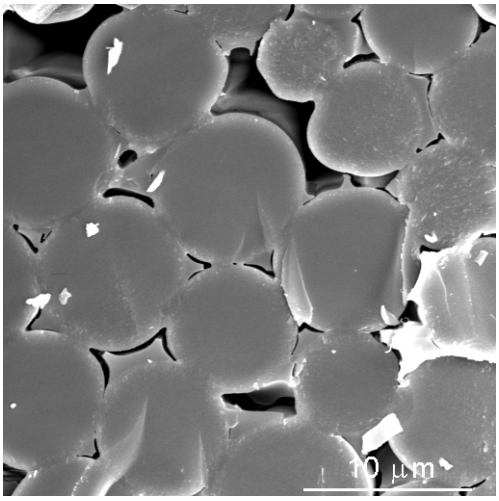

Fig. 15 Fibre coalescence (B1 with lubricated fibres, pyrolysed and oxidised at 750 °C).

One feature of the fracture is typical for the KV fibres, namely the proneness to break in very *complex modes*. Especially in the composites with the M130-derived matrix the propagating crack cuts the fibre cross-section in different directions and in a non-planar way (Fig. 16, Fig. 18, Fig. 20 and Fig. 22). This feature was not observed with the Basaltex fibres. Fig. 17 reveals the extent of a monolithic behaviour: the fracture plane cuts the fibres in an oblique direction, not distinguishing between fibres and matrix.

Further photographs present more cases of cracks parallel to or slightly inclined to the fibre axis (Fig. 19, Fig. 21).

A very specific appearance of the inner part of fractured specimens was observed in the composites made from the KV fibres (both the lubricated and de-lubricated ones) and M130 resin. In those oxidized at 750 °C a large amount of open *caverns* exists

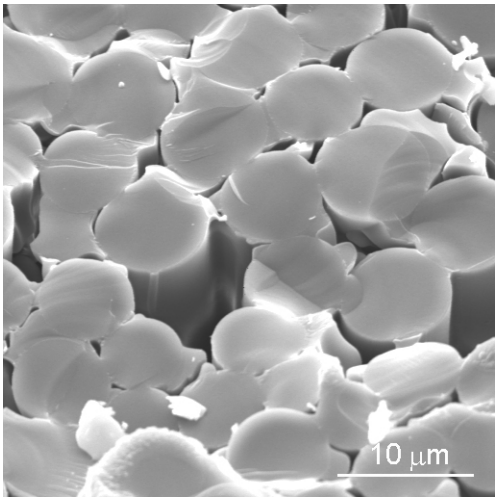

Fig. 16 Fracture of fibres (KV2 with de-lubricated fibres, pyrolysed and oxidised at 750 °C).

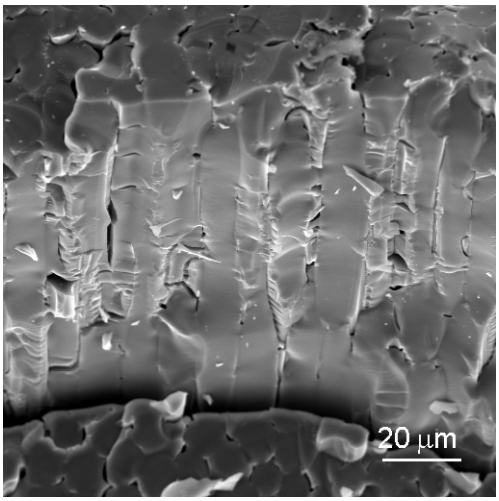

Fig. 17 Oblique fracture across the fibres (KV2 with lubricated fibres, pyrolysed and oxidised at 750 °C).

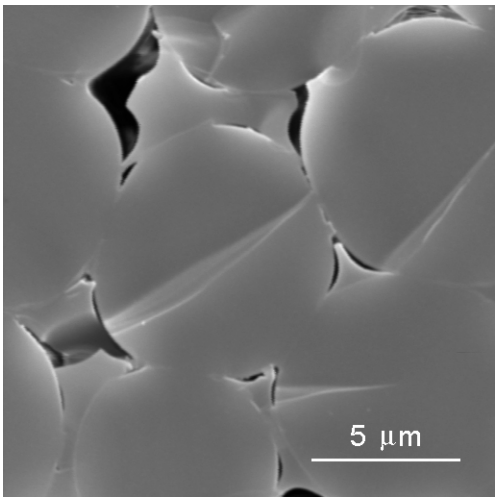

Fig. 18 Complex shape of the fractured fibres **(**KV1 with lubricated fibres, pyrolysed and oxidised at 650 °C).

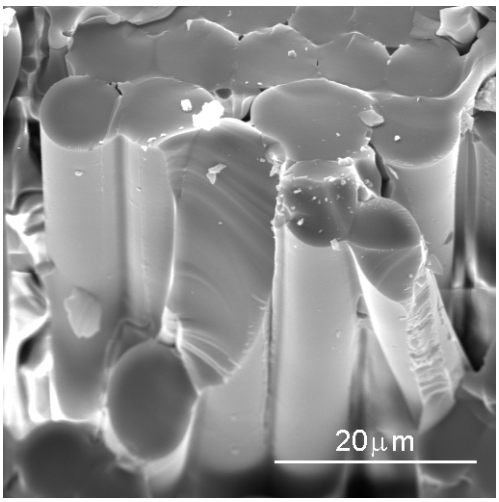

Fig. 19 Oblique fracture of the fibre (KV2 with lubricated fibres, pyrolysed and oxidised at 650 °C).

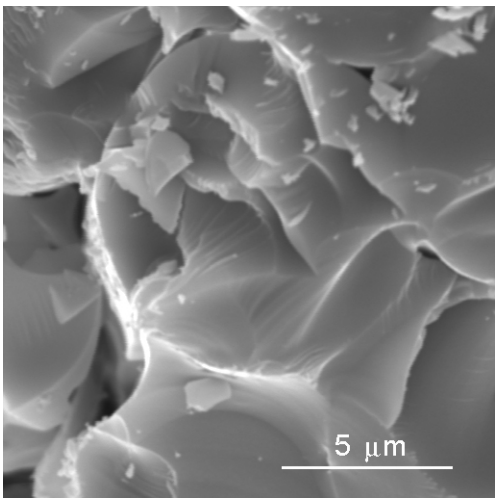

Fig. 20 A very complex shape of the fibre fracture (KV2 with lubricated fibres, pyrolysed and oxidised at 650 °C).

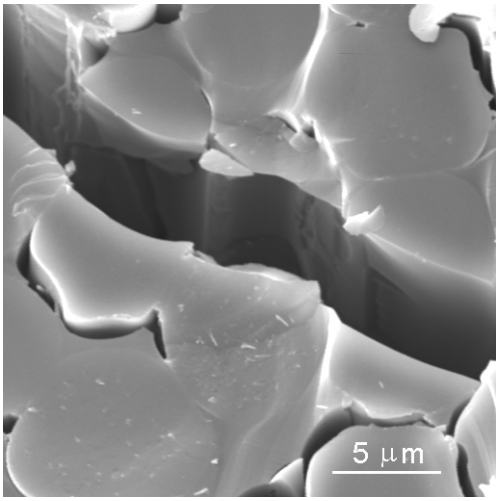

Fig. 21 Crack splitting the fibres (KV2 with lubricated fibres, pyrolysed and oxidised at 750 °C).

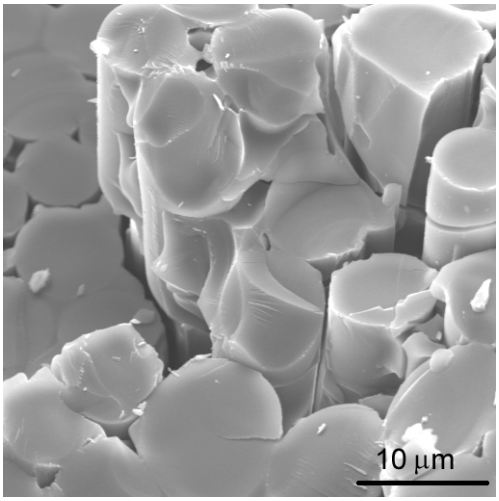

Fig. 22 Inclined fracture of the fibres (KV2 with delubricated fibres, pyrolysed and oxidised at 750 °C).

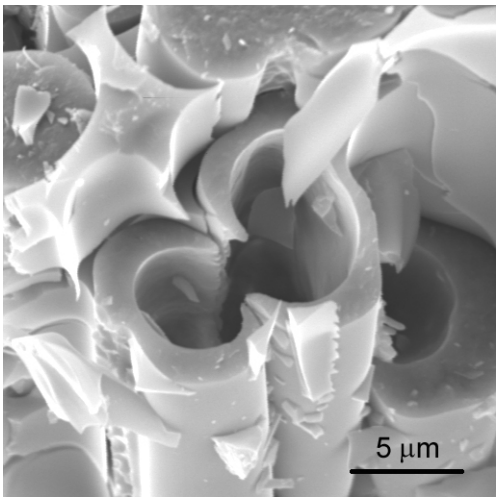

Fig. 23 Caverns inside the fibres (KV2 with delubricated fibres, pyrolysed and oxidised at 750 °C).

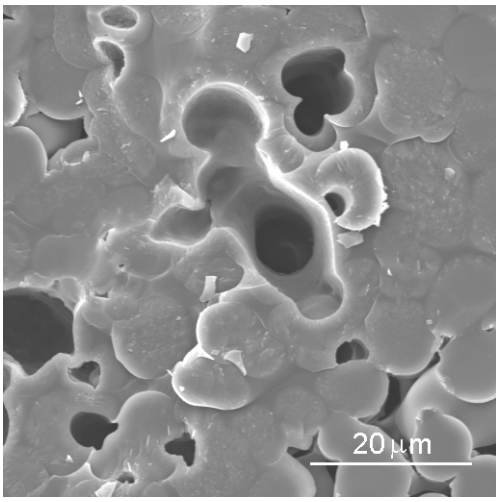

Fig. 24 Caverns at the fracture surface (KV2 with delubricated fibres, pyrolysed and oxidised at 750 °C).

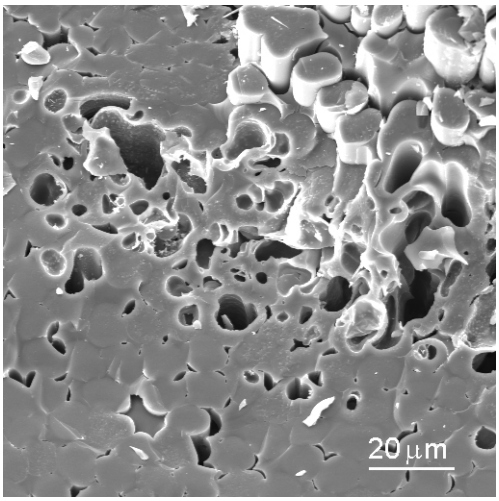

Fig. 25 Caverns at the fracture surface (KV2 with lubricated fibres, pyrolysed and oxidised at 750 °C).

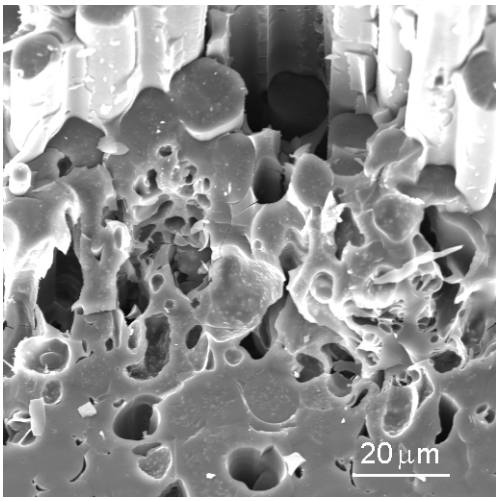

Fig. 26 Caverns at the fracture surface (KV2 with lubricated fibres, pyrolysed and oxidised at 750 °C).

impinging upon both matrix and fibres (Fig. 23, Fig. 24, Fig. 25 and Fig. 26). Possibility of an inherent origin of the caverns is very improbable because the composites in question are made from different prepregs and their manufacture processes have no point of contact. Therefore, there should exist some common reason for cavern occurrence, which is independent of possible manufacture flaws. As a working hypothesis an enhanced permeability of these materials to gas (perhaps a system of open, communicating pores) can be proposed.

In many cases the fracture discloses the *appearance of individual fibres*, which varies broadly from total bareness (Fig. 27) through partial coverage by minute flakes (Fig. 28) to massive coverage with matrix blocks (Fig. 29).

The bare fibres are found mostly (but not exclusively) in the composites made with de-lubricated fibres (Fig. 30, Fig. 31, Fig. 32).

The fibre surface is sometimes undulated (Fig. 33, Fig. 34) but it is difficult to decide on the nature of the undulated surface. The case depicted in Fig. 35 may result from some reaction with the matrix.

A very specific appearance of the fibre surface can be found in the composites reinforced with lubricated KV fibres in combination with the L901-derived matrix (Fig. 36 and Fig. 37). The high surface roughness gives evidence on a strong interaction with the matrix.

It was interesting to find out whether the appearance of fibre surfaces is due solely to their

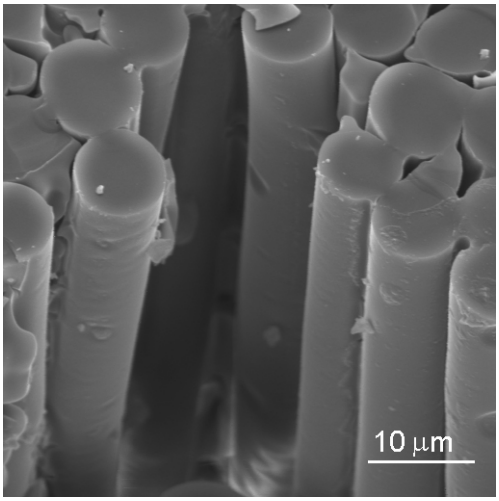

Fig. 27 Bare fibres (KV1 with delubricated fibres, pyrolysed and oxidised at 650 °C).

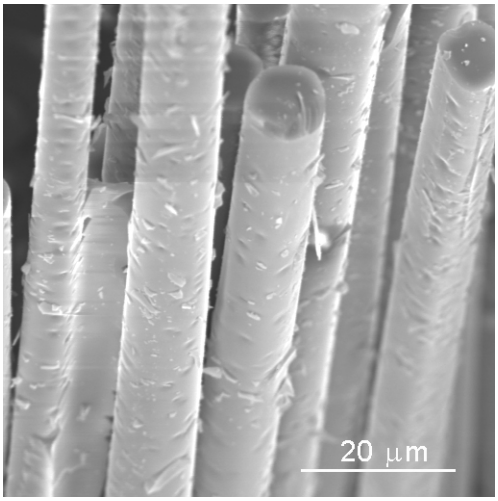

Fig. 28 Fibres covered by flakes (B2 with delubricated fibres, pyrolysed and oxidised at 650 °C).

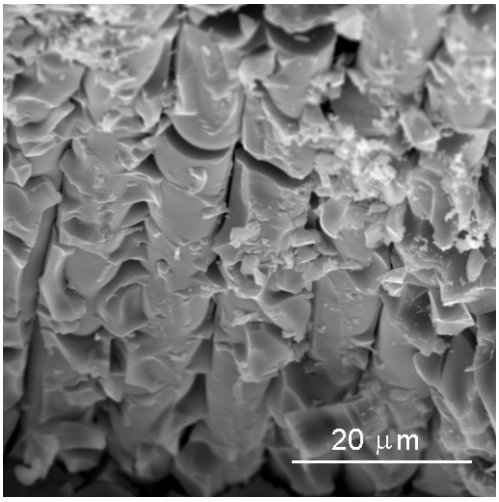

Fig. 29 Fibres with blocks of adhering matrix (B1 with delubricated fibres, pyrolysed and oxidised at 750 °C).

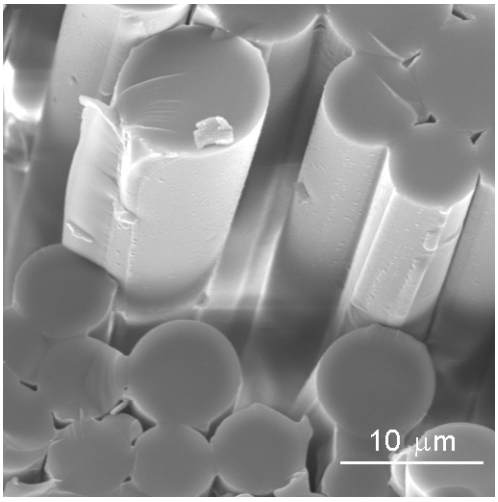

Fig. 30 Surface of the delubricated fibres (KV2 with delubricated fibres, pyrolysed and oxidised at 750 °C).

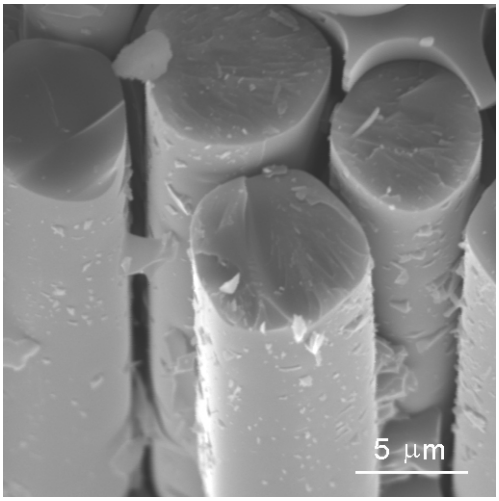

Fig. 31 Surface of the delubricated fibres (B1 with delubricated fibres, pyrolysed and oxidised at 650 °C).

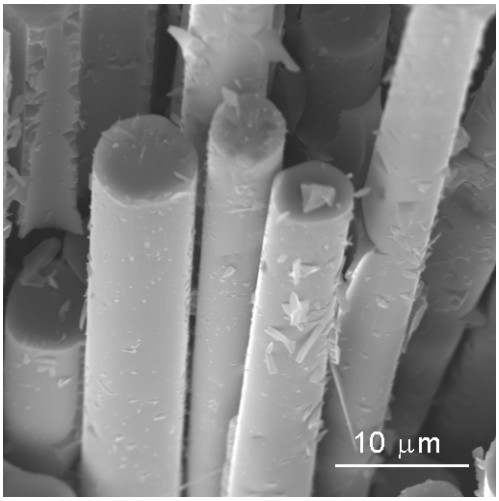

Fig. 32 Surface of the delubricated fibres (KV2 with delubricated fibres, pyrolysed and oxidised at 650 °C).

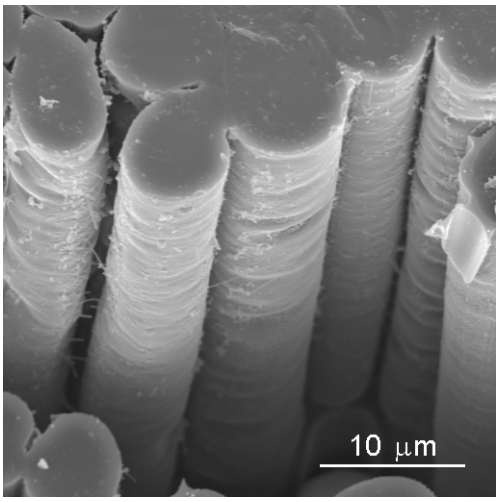

Fig. 33 Undulated fibre surface (KV1 with lubricated fibres, pyrolysed and oxidised at 750 °C).

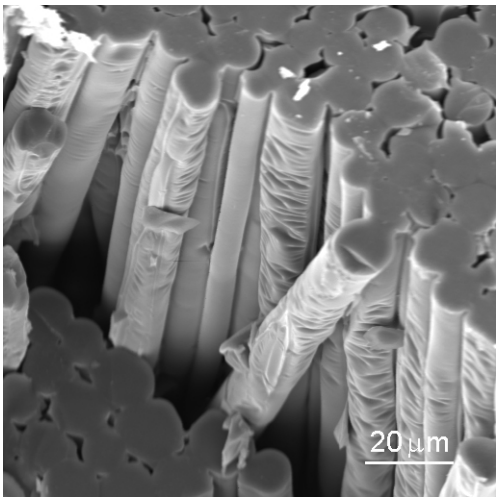

Fig. 34 Undulated fibre surface (B1 with delubricated fibres, pyrolysed and oxidised at 750 °C).

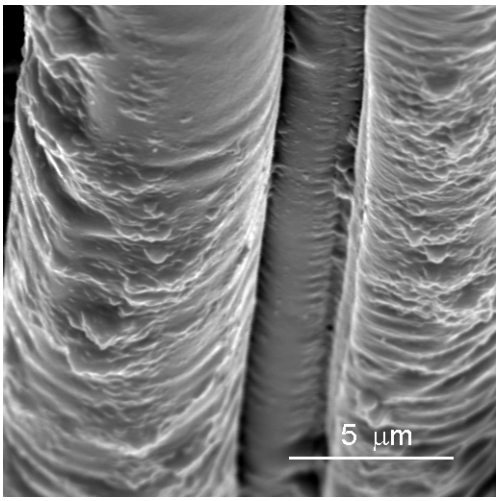

Fig. 35 Fibre surface with possible reaction product deposit (B2 with delubricated fibres, pyrolysed and oxidised at 750 °C).

thermal treatment or whether it results from the interaction with matrix in the thermally treated composites. For this purpose an *additional investigation of the fibre*s alone, which were treated in the same way as those embedded in the composite specimens, was undertaken. In all cases the fibre surfaces were smooth and clean (Fig. 38, Fig. 39, Fig. 40) suggesting thus that the presence of matrix is a key factor in formation of the surfaces like those in Fig. 35.

DISCUSSION AND CONCLUSIONS

It is desirable to analyze the fracture behaviour from the causal viewpoint, i.e., to identify the influence of: *a)* the choice of raw materials (i.e., fibre and matrix type) and *b)* the processing temperature on the resulting appearance of the fracture surface.

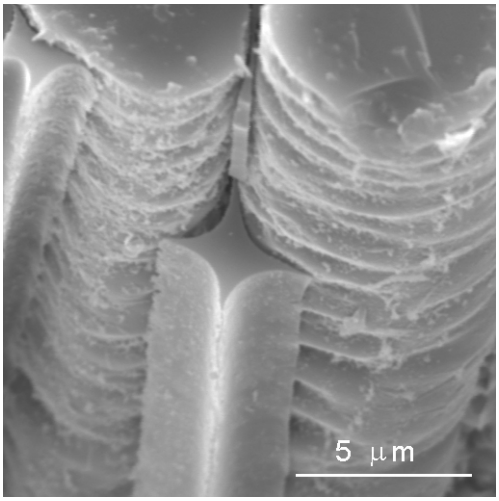

Fig. 36 Fibre-matrix bonding (KV1 with lubricated fibres, pyrolysed and oxidised at 750 °C).

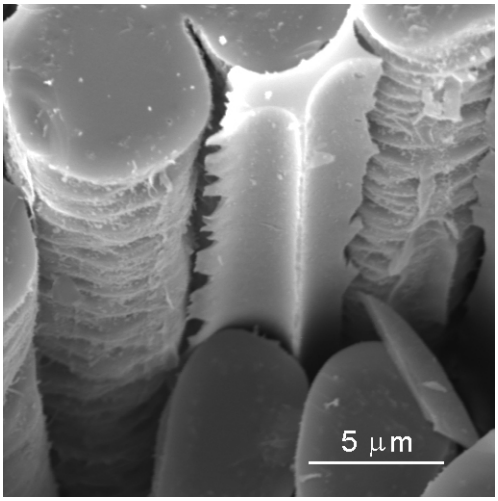

Fig. 37 Fibre-matrix bonding (KV1 with lubricated fibres, pyrolysed and oxidised at 750 °C).

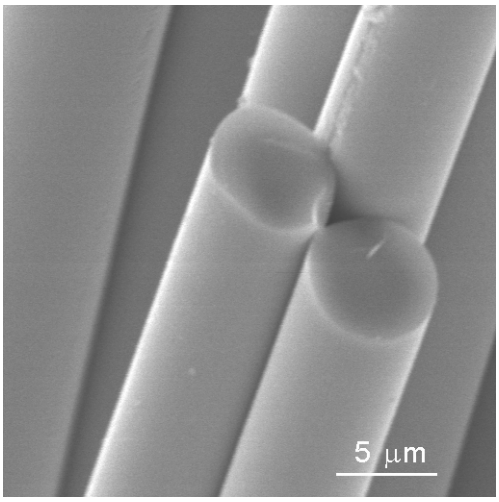

Fig. 38 The KV fibres pyrolysed at 750 °C.

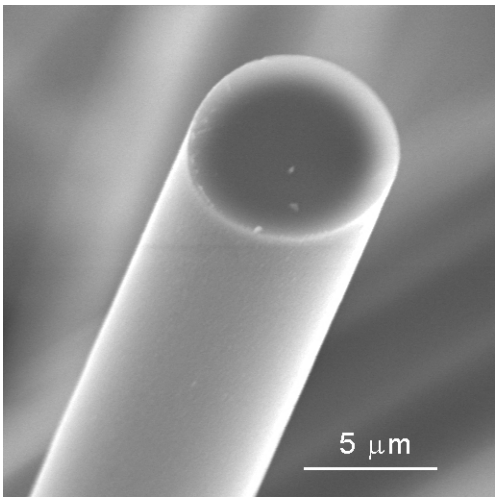

Fig. 39 The KV fibres pyrolysed at 750 °C and oxidized 4h at the same temperature.

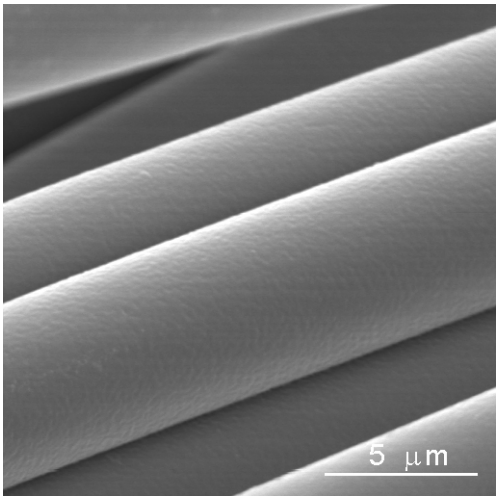

Fig. 40 The KV fibres pyrolysed at 750 °C and oxidized 4h at the same temperature.

Attempts were made to trace the influence of the treatment temperature and/or the surface state of fibres (existence/non-existence of lubrication) on the fracture behaviour but the results are not convincing, as the investigated fracture surfaces are qualitatively similar.

Very few conclusions can be drawn from the acquired results:

- Some features are common to a vast majority of the investigated materials, e.g., a very low occurrence of fibre pull-out and fibre coalescence. These are chiefly responsible for the observed brittle fracture.
- Other features are restrained to certain composite types:

1. undulation of the disclosed fibre surface exists only in the composites pyrolysed and treated in air at 750 °C (Fig. 33, Fig. 34, Fig. 35). This treatment temperature and its duration are to be blamed.
2. breaking of individual fibres in a very complicated mode (including cracking parallel to the fibre axis) occurred only with the KV fibres, predominantly in combination with the M130 matrix.
3. failure by delamination took place only with the B130 composites treated to 650 and 750 °C, which both stem from the same prepreg stacking. It suggests that flaws in the lay-out of the prepreg can be a common reason for the delamination behaviour.

We have also attempted to relate the measured mechanical properties (strength, moduli) to the level of occurrence of voids in the fracture surface (the feature allowing a rough quantification from the SEM images). The hypothesis was a simple one: the larger is the void fraction the lower should be the modulus or strength. It was but partially proved for the composites with the M130-derived matrix (B130, KV130) pyrolysed and oxidized at 650 °C, which generally possess less voids than those with the L901-derived one. Within the composites treated to 750 °C, those with the M130-derived matrix also possess no or a small amount of voids (in contrary to the composites with the L901- derived matrix) but no dependence of the mechanical parameters on the void content was established. The mechanical properties are obviously governed by other factors (fibre volume fraction, interface strength and properties, etc.).

To conclude, the investigated composites (pyrolysed polysiloxane matrix with basalt fibre reinforcement) worsened their properties after treatment in air at elevated temperature (650 – 750 °C). The originally non-catastrophic flexural failure (Fig. 6) changed to a brittle fracture, which was accompanied with a flexural strength decrease (Fig. 5). The coalescence of fibres (Fig. 14, Fig. 15) and their strong interaction with the matrix (Fig. 29, Fig. 35) are probably the main reasons for the onset of brittleness. Unless these drawbacks are resolved (perhaps, by proper surface treatment of basalt fibres aiming at optimization of the fibre/matrix interaction and a better soaking of the fibre tows) the service temperature of the composites in air will probably not exceed approximately 500 °C.

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