

INFLUENCE OF THE ORGANIC/INORGANIC PYROLYSIS CONVERSION LEVEL ON MECHANICAL PROPERTIES OF COMPOSITES WITH E-GLASS OR BASALT FIBRE REINFORCEMENT

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Unidirectional fibre reinforced composites were prepared, with polysiloxane matrix converted pyrolytically to silicon oxycarbide to a varying degree depending on pyrolysis conditions. As reinforcement, continuous E-glass or basalt fibres were used in order to compare their eventually different effect in the composites. The samples were made from wet-wound prepregs and first cured at 180-250°C and thereafter pyrolysed at 420-750°C. Flexural strength, Young's and shear moduli of the final composites were measured. The curing of the siloxane resin at lower temperatures was investigated by thermogravimetry. After pyrolysis, the reinforcing fibres were characterized by light microscopy in order to assess their eventual deformation and damaging at elevated temperatures. The composites pyrolysed at the highest temperatures differ very strongly in flexural strength but not in moduli. The low strength of the glass-reinforced composites is due to their brittle failure and is obviously caused by strong fibre-matrix bonding, while the high strength of the basalt reinforced ones results from a weak bonding which makes fibre pull-out possible. The tendency to fibre pull-out was evaluated by comparing loading characteristics of the samples. A probable explanation of the different fibre bonding tendency is suggested, based on reactivity comparison of iron-containing and iron-free silicates with silica.

INTRODUCTION

Polymer matrix composites can perform only to limited temperatures and cannot be compared to performance of metals or ceramic materials. Another limitation of their application potential consists in low fire endurance and fire safety because of their toxic combustion products. Therefore the effort to develop suitable inorganic matrices in order to solve these problems is always actual. Numerous preparation routes of metal, silicate or ceramic matrix composites [1] were described. Another group of composite materials are C-C composites whose reinforcing carbon fibres are embedded in a carbon matrix originating in a pyrolysed precursor polymer or pitch [2]. This preparation route can be extended also to precursors whose pyrolysis residue is other than carbon matter. One of the most promising possibilities is the pyrolysis of polysiloxane resins, known to yield a glassy noncrystalline matter of various ratios of Si-O-C, "silicon oxycarbide", which is quite devoid of organic groups. This topic is addressed in a recent work of the authors [3], where the elemental ratio and chemical bonding in Si-O-C from pyrolysed

methylphenylsiloxane and methylsiloxane resins was evaluated by NMR spectroscopy after pyrolysis at different temperatures.

The methylsiloxane precursor resin was used by the authors for laboratory production of partially pyrolyzed composites with basalt fibres [4], where strength, fracture toughness and elastic constants were investigated at room and at elevated temperatures. The mentioned study revealed remarkable properties of the composite prepared by partial pyrolysis at 650 °C, especially higher mechanical strength and fracture toughness than those made at other pyrolysis temperatures or cured only (180–250°C) ones.

In an earlier investigation, the authors have shown [5] that E-glass fibres (made by S.Gobain Vetrotex) outperform basalt fibres in thermal resistance because no recrystallization takes place in the former ones up to 750°C, which is not the case with basalt fibres. It is therefore interesting to compare properties of mutually similar composites with pyrolyzed methylsiloxane matrix which differ in the type of reinforcing (silicate) fibres being basalt or glass. This comparison is the topic of the presented work.

EXPERIMENTAL

The investigated composite samples were unidirectionally reinforced with rovings of either basalt fibres Kamenny Vek or E-glass fibres from S.Gobain Vetrotex (see Table 1 and Table 2), embedded in polydimethylsiloxane resin Lukosil M130 (Lučební závody Kolín, Czech Republic). This was achieved by stacking of 8 layers of basalt prepreg or 10 layers of E-glass prepreg made by wet winding, followed by pressing and hot curing of the stack in a heated open mould.

For curing no catalyst was used. The curing of the composite took place under a controlled pressure-temperature regime with the aim that the evolution of the gaseous products of the proceeding reaction did not damage the cured body.

Curing of polysiloxane resins is accompanied by evolution and release of water vapour produced by silanol condensation. Kinetics of the curing process of the dried Lukosil M130 resin was therefore studied by thermo gravimetric analysis in air under heating rate 1.5 K/min at 20-300°C. The heating run was repeated three times in order to distinguish curing itself from thermal or oxidizing degradation of polymer.

The TGA graphs show that most of the mass loss, and hence of branched siloxane resin curing to polysiloxane network occurs during the first scan (ca. -5 wt.%) with only relatively small mass loss at second scan (-1.5 wt.%), while at the third scan the mass loss is negligible (Figure 1a). The decreasing mass loss at 300°C rules out eventual progressing degradation or oxidation.

From the first derivative of the TGA curves (Figure 1b) it can be inferred that the water release is confined to 100–250°C. During curing of the investigated composites the heating rate was therefore lowered to 0.5 K/min between 100 and 250°C.

The (cured) prepolymer composite bodies were examined for open porosity P and density ρ by the boiling water method [7]. Their fibre volume content V_f was determined from the weight and dimensions of the body, the known amount of fibres embedded in it, and densities of fibres (basalt: 2540 kg/m³, E-glass: 2600 kg/m³) and cured resin 1220 kg/m³. The following values were found for the cured basalt composite: $P = 5 \pm 1 \%$, $\rho = 1980 \pm 40 \text{ kg/m}^3$, $V_f = 65 \pm 3\%$, while the cured glass composite yielded $P = 12 \pm 4 \%$, $\rho = 2010 \pm 80 \text{ kg/m}^3$, and $V_f = 70 \pm 3\%$.

Table 2. Chemical composition of the fibres used as determined in our previous work [5].

	basalt measured (wt.%)	E-glass measured (wt.%)
SiO ₂	53.6	53.5
TiO ₂	1.1	0.3
Al ₂ O ₃	17.4	13.6
Fe ₂ O ₃	4.7	0.2
FeO	4.4	0.2
MnO	0.1	0
MgO	4.1	1.2
CaO	8.5	21.4
Na ₂ O	2.6	0.5
K ₂ O	1.6	0.5
P ₂ O ₅	0.2	0.1

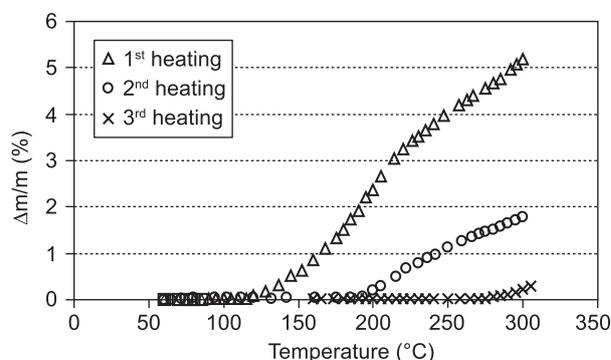


Figure 1a. Thermogravimetric diagram of the curing process of polymethylsiloxane resin M130.

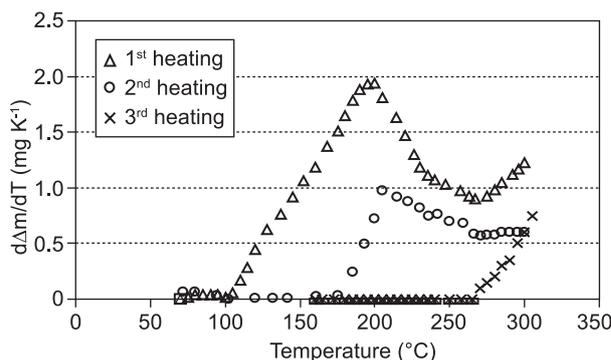
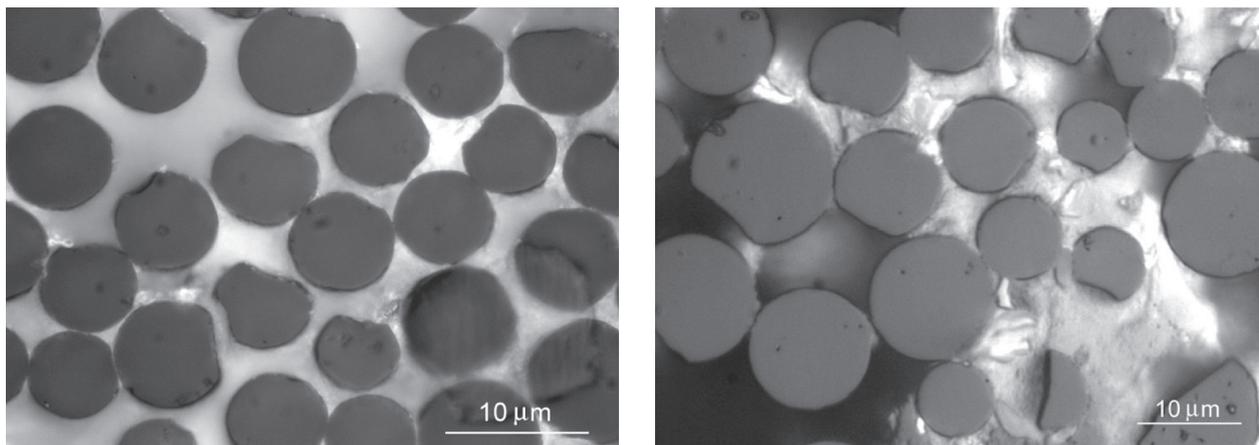


Figure 1b. The 1st derivative of the TGA with respect to temperature.

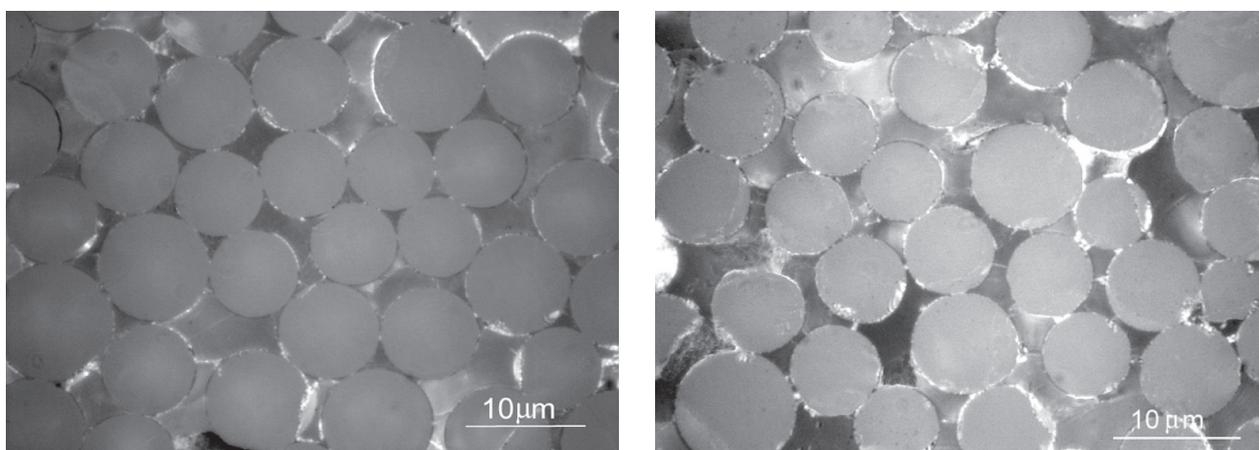
Table 1. Basic properties of the used basalt and E-glass fibres.

		grade	linear density (tex)	average fibre cross-section (µm ²)	tensile strength (MPa)	tensile modulus (GPa)
Kamenny Vek	www.basfiber.com	KV13	320	130	2480*	76**
S. Gobain Vetrotex	www.vetrotextextiles.com	RO99	292	145	3400***	73***

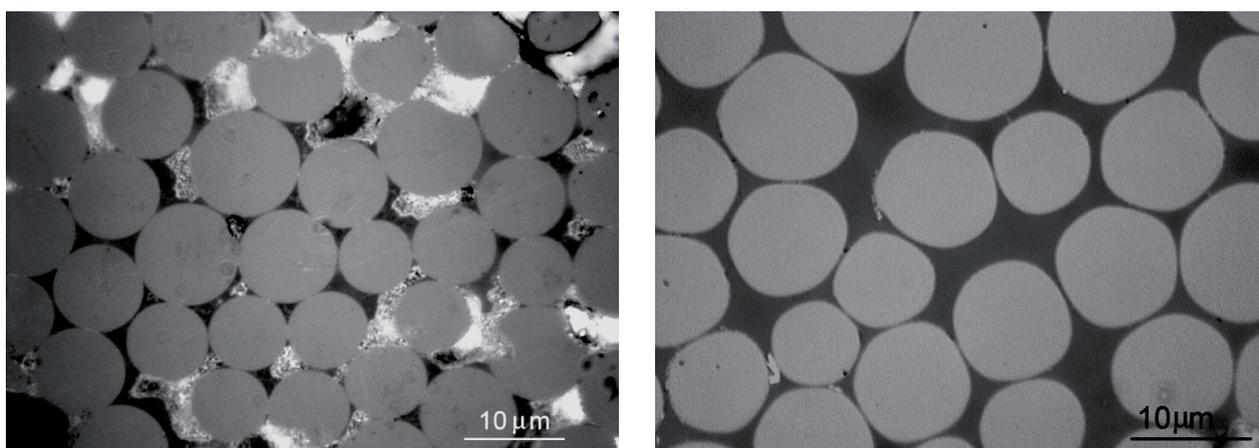
* [6], ** [4], *** S. Gobain Vetrotex Datasheet



a) 420°C



b) 550°C



c) 650°C

E-glass

basalt

Figure 2. Light microscopy photographs of the studied composites subjected to: a) pyrolysis at 420°C, b) pyrolysis at 550°C, c) pyrolysis at 650°C.

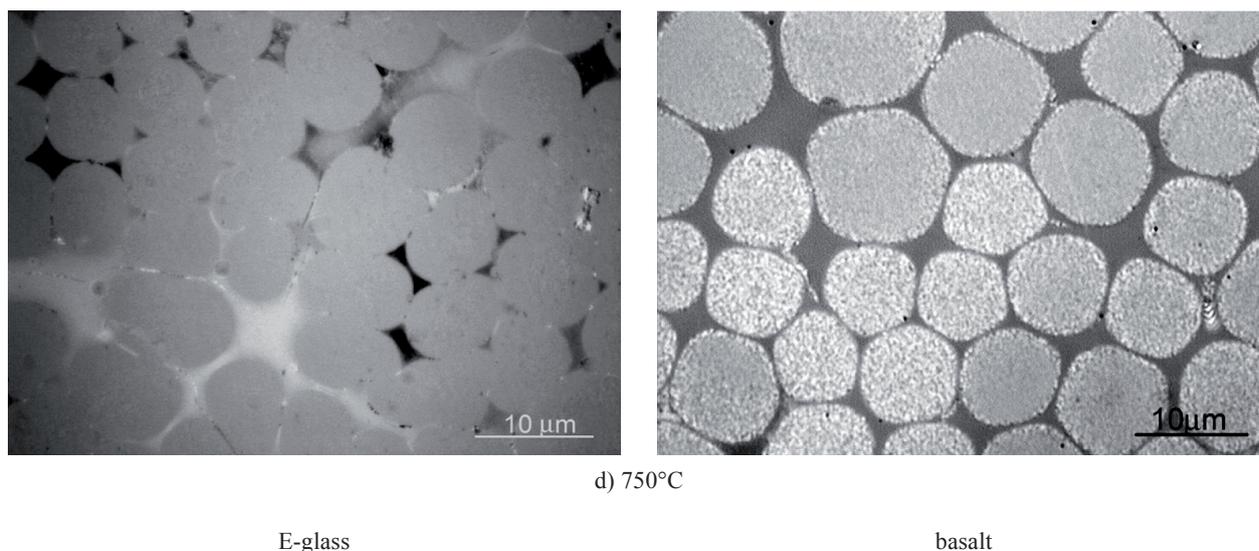


Figure 2. Light microscopy photographs of the studied composites subjected to: d) pyrolysis at 750°C.

Finally, the composite samples were pyrolysed in a protecting atmosphere of nitrogen (a chemical reactivity of nitrogen is not expected here). In order to explore the influence of the achieved organic – inorganic conversion level of the matrix on the mechanical properties, several controlled temperature courses of pyrolysis were applied for the specimens' preparation. Ultimate temperatures of these courses were 420, 550, 650 and 750°C, the heating rate was 50 K/h until 420°C and 10 K/h above this temperature. The dwell on respective final temperatures was 10 hours invariably; the subsequently applied cooling rate was -50 K/h.

The effect of the maximum pyrolysis temperature on the composite structure can be observed in light microscopy photographs (Figure 2). The composites partially pyrolyzed at 420°C (Figure 2a) contain numerous voids and some bare fibres. At higher pyrolysis temperatures (550, 650, and 750°C) the packing of reinforcing fibres is by far more regular. The detailed appearance of the fibres in the composite with basalt fibres pyrolyzed partially at 750°C (Figure 2d) indicates a commencing formation of crystalline phases [5]. It can be further observed that plastic deformation of the fibres resulting in deviation from their originally circular cross-section begins at 650°C for the basalt-reinforced composites but not for the glass-reinforced ones. At 750°C, however, the basalt fibres become almost polygonal and the glass fibres reveal a well-pronounced deformation.

Composite characterization methods

Experiments compared the composites reinforced with basalt or E-glass fibres and pyrolysed to 420, 550, 650, and 750°C, as well as the cured only composites of both types. Flexural strength in 3-point bending R_m ,

Young's modulus E and shear modulus G of the composite samples were measured at laboratory temperature (25°C). Flexural strength was measured using the universal testing machine Inspekt 100 (made by Hegewald-Peschke, Germany), Young's modulus and shear modulus were measured using the resonant frequency tester Erudite (CNS Electronics Ltd., London, UK) at frequencies up to 100 kHz and evaluated according to [8]. Dimensions of rectangular samples were $2 \times 4 \times 50$ mm. Six samples of any batch were subjected to (non-destructive) resonant frequency measurement and, finally, they were tested to flexural strength. Average values and standard deviations are plotted in the corresponding graphs (Figures 3-5).

RESULTS AND DISCUSSION

The results of Young's moduli E comparison reveal generally an expected course. The moduli do not change strongly with the pyrolysis temperature, although at 750°C a moderate increase is clearly achieved (up to 70 GPa with basalt fibres). A shallow minimum can be found for the composites with E-glass fibres pyrolysed partially to 420°C (Figure 3). The established trend is valid also for the basalt fibre composites.

The shear modulus G (Figure 4) of the composites prepared rises very sharply at the highest pyrolysis temperatures and achieves 3-4 times higher values if compared to those of the cured only samples.

The shear modulus, as illustrated in Figure 4, is much more sensitive to the matrix discontinuities and compliances in the tested samples. Obviously, G achieves high values, after pyrolysis at higher temperatures, where the matrix is to a high degree transformed from the softer siloxane network to the stiffer and stronger cross-linked almost ceramic silicon oxycarbide, which is compactly

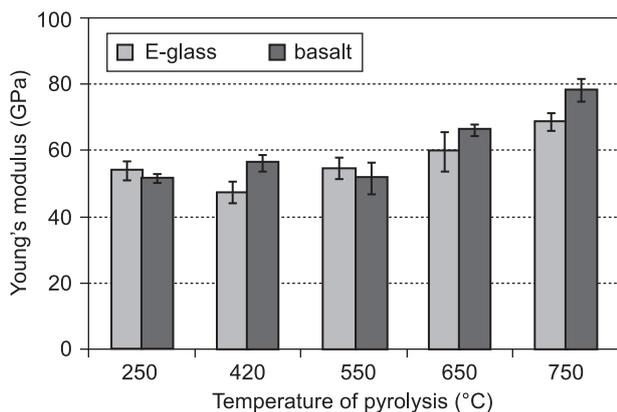


Figure 3. The influence of final pyrolysis temperature on Young's modulus of composites with basalt fibre and E-glass fibre reinforcement.

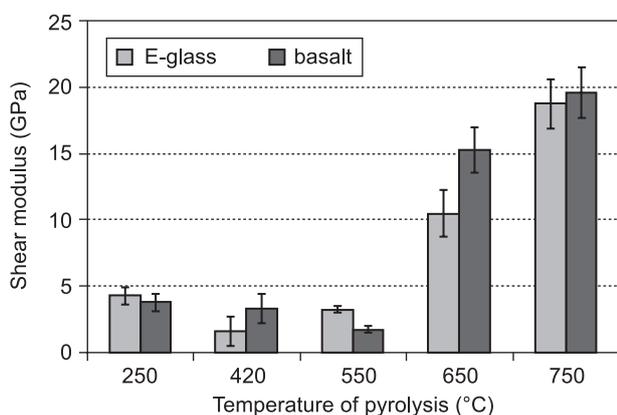


Figure 4. The influence of final pyrolysis temperature on shear modulus of composites with basalt fibre and E-glass fibre reinforcement.

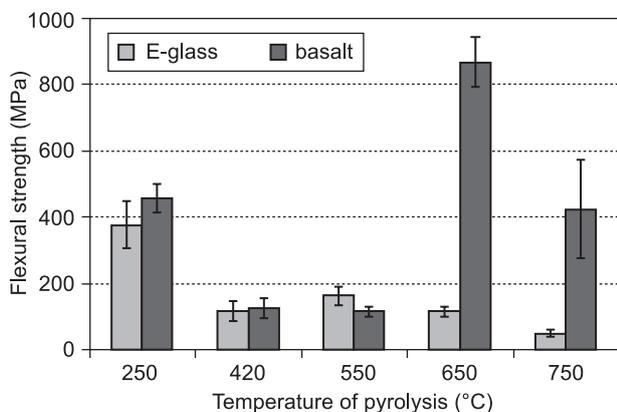


Figure 5. The influence of final pyrolysis temperature on flexural strength of composites with basalt fibre and E-glass fibre reinforcement.

arranged around the reinforcing fibres, in contrast to the porous matrices only partly pyrolyzed at the lower temperatures.

The flexural strength R_m of the composites cured at 250°C (not pyrolysed) equals approximately 400 MPa for both the basalt and E-glass reinforced composites (Figure 5)

For the partially pyrolysed basalt fibre composites the R_m depends considerably on the ultimate pyrolysis temperature. The samples pyrolysed at 420 °C exhibit the lowest value of R_m (approximately 110 MPa). Values of R_m increases significantly after pyrolysis to 650°C and achieve a maximum of more than 800 MPa (Figure 5), almost twice of the R_m of the cured only (250°C) composite. The basalt reinforced material retains acceptable strength (\approx 400 MPa) also after pyrolysis to 750°C.

The flexural strength of partially pyrolysed E-glass fibre composites depends on the ultimate pyrolysis temperature in a different way. Again, the flexural strength R_m after pyrolysis at 420°C exhibits a very low value (Figure 5) and it reveals also a very weak maximum at the pyrolysis temperature of 550°C. Pyrolysis to higher temperatures (650 and 750°C) leads to renewed fall of flexural strength to values much less than those exhibited by the corresponding basalt fibre reinforced composite or those prior to pyrolysis (only cured at 250°C).

The obtained results of flexural strength R_m in dependence of pyrolysis temperature for both composite types reveal a common feature, namely an abrupt fall from \approx 400 MPa (cured only state) to \approx 110MPa (partially pyrolysed at 420°C state). This fall in R_m can be explained by the actual condition of the matrix (Figure 2a). At 420°C the matrix is in the middle of organic/inorganic conversion, which causes its embrittlement, volume shrinkage up to 40 %, and void formation. The defective matrix cannot sufficiently support the reinforcing fibres and transfer the stresses which results in the loss of strength.

Even after pyrolysis at 550°C the R_m remains low though the matrix contains less cracks and voids. The mutual support of matrix and fibres still seems to be too weak due to uncompleted organic-inorganic conversion of the matrix. At still higher levels of the polymer/ceramic conversion, i.e. at ultimate pyrolysis temperatures 650 and 750°C the both types of composite behave totally differently. The basalt fibre reinforced one reveal a surprising rise of flexural strength to values over 800 MPa at 650°C which testifies to very well matched properties at the fibre-matrix interface. Also at 750°C the R_m yields a still satisfying value (\approx 400 MPa); the decrease from its value at 650°C may be caused by embrittlement of basalt fibres, which is due to the change of their microstructure (namely crystallisation) as illustrated in Figure 2d and also in [5].

In contrast to the basalt composites, the strength of the E-glass reinforced composite continues to fall

at 650 and 750 °C, where very low values of R_m (≈ 50 MPa) are found. It should be mentioned that no indicia of commencing crystallization in E-glass fibres even at 750°C were detected by us (see Figure 2d and [5]) as, generally, glass has a very low tendency to crystallization upon heating. Hence, the E-glass fibres in the tested composites could not have become fragile and thus reduce the flexural strength. Moreover, as already mentioned above, E-glass fibres reveal higher thermal stability and their degradation cannot be expected at 650-750°C.

The very big difference between the flexural strength of E-glass reinforced and basalt-reinforced composites pyrolysed to 650 and 750°C is a highly interesting result. A hint for explaining it can be found in a striking difference of their failure mode. As seen in Figure 6, after partial pyrolysis to 750°C the E-glass composites fail in a brittle manner while the basalt ones fail stepwise and non-catastrophically.

Obviously, the E-glass fibres (after 650 and 750°C pyrolysis) show a much higher adhesion to the matrix and break suddenly together with the matrix if loaded,

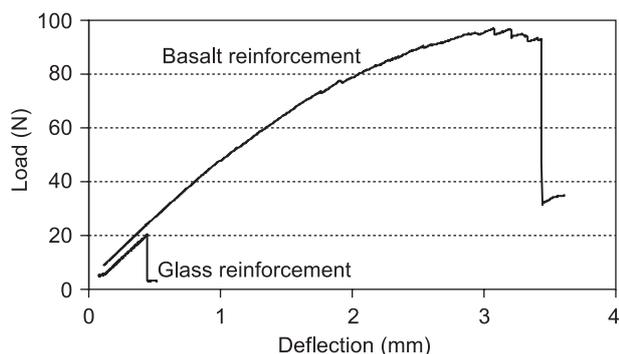


Figure 6. Loading characteristics of composites with basalt fibre and E-glass fibre reinforcement pyrolysed partially to 650°C.

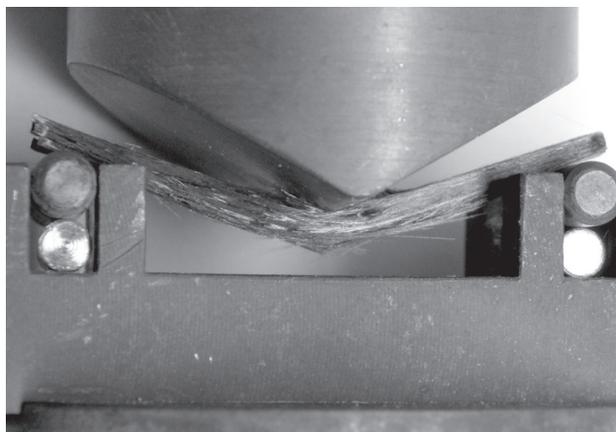
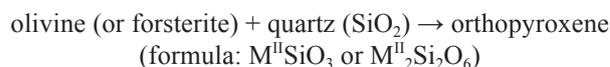


Figure 7. Sample of basalt fibre composite partially pyrolysed to 650°C after completion of the 3-point flexural test.

while basalt fibres more easily separate from the matrix and maintain their integrity even when bent after failure (Figure 7). The reason for this difference could be found in a more inert behaviour of basalt with respect to silica which probably might be a component of the SiOC matrix. Indeed, according to more recent research, the SiOC matrix most likely contains nanometer-scaled SiO₂ domains [9], [10], [11], which are of key importance for the matrix interaction with silica and silicate materials. The SiOC glasses are typically nano-heterogeneous [9], [10], with molecular-sized domains of several nanometers width, consisting of SiC, SiO₂ and mostly also of carbon inclusions. The nano-domains act as nuclei of the observed micro-phase separation in SiOC at temperatures above 1000°C, where the atom mobility becomes sufficiently high. On the other hand, homogeneous SiOC networks can be prepared by rf-magnetron sputtering methods [11], which were not used in our synthesis.

The used basalt fibres contain a considerable amount of iron(II) and iron(III) oxide as shown in Table 2 (the component contents in E-glass and basalt were determined in [5]) describing the fibre composition. From literature it is known [12], [13] that fayalite (Fe₂SiO₄) is stable in contact with quartz (silica) at elevated temperatures and low pressures, whereas forsterite (Mg₂SiO₄) or olivine (Mg_{2-x}Fe_xSiO₄) react at the same conditions according



Hence, increasing iron(II) oxide content generally stabilizes the Mg_{2-x}Fe_xSiO₄ silicate against reaction with SiO₂, and more vigorous conditions are then needed to enforce the reaction. If fayalite is oxidized (namely Fe^{II} to Fe^{III}) it decomposes to the constituent oxides, instead of Fe^{III} orthosilicate, which is not stable due to too high acidity of the Fe^{III} oxide:



The magnetite (Fe₂O₃) then separates in form of small particles dispersed in SiO₂. An analogous behaviour is displayed by other Fe-containing silicates. A content of Fe₂O₃ hence also does not improve the affinity of a material towards silica. The mentioned reversible redox reaction of fayalite is known in the literature as “FMQ” (fayalite-magnetite-quartz) oxygen buffer.

The above described behaviour of FeO and Fe₂O₃ in silicates makes it clear, that an elevated content of iron oxides (both Fe^{II} and Fe^{III}) in a silicate generally reduces its reactivity with silica.

As mentioned above, silica is a likely nano-component of the SiOC matrix, and due to chemical considerations is most responsible for interactions with the silicate-based fibres. The presence of silica as fibre-bonding component in the matrix and of iron oxides as bonding inhibitors in the basalt fibres hence well explain their more inert behaviour compared to E-glass.

CONCLUSIONS

Though apparently similar, E-glass fibres and basalt fibres strongly differ in their behaviour as reinforcement in heat resistant silicon oxycarbide (SiOC) composites made by partial pyrolysis of polysiloxane matrix at over 650°C. The basalt composites reveal high flexural strength (over 800 MPa) due to lowered fibre-matrix bonding and non-catastrophic failure mode. Much lower flexural strength of the E-glass reinforced composites (less than 100 MPa) can be attributed to their brittleness caused by strong fibre-matrix bonding. A suggested tentative explanation of these results is based on inertness of basalt, which is supported by behaviour of iron oxides in silicates, which is notorious in literature.

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