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Influence of pyrolysis temperature on fracture response in SiOC based composites reinforced by basalt woven fabric

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Abstract

The fracture resistance of ceramic based composites reinforced by various ceramic fibres can be dramatically enhanced when an efficient fracture mechanism takes place during the crack propagation. Presented work shows an effect of the pyrolysis temperature of the composite matrix on the fracture behaviour of the composite. The matrix is formed from the polysiloxane resin precursor and the reinforcement is a basalt woven fabric. The temperature range under investigation was from 600 °C, where the onset of fracture properties were observed up to 800 °C. Above this temperature basalt fibres suffer by rapid degradation of the microstructure. The optimum stage of the polysiloxane resin transformation maximizing the fracture resistance of the composite was identified. The fractographic analysis of the fracture surfaces revealed the differences in the acting fracture mechanism.

Keywords: Fracture behaviour; CMCs; Pyrolysis; Basalt fibre; Polysiloxane

1. Introduction

Composite materials using long fibres as a reinforcement are widely used in many applications. The majority of such composites use a polymer matrix reinforced by long fibres and usually are used in the shell form, e.g. airframes, car body, windmills, building parts etc., and they are known as fibre reinforced polymers (FRP) or more specifically utilizing carbon fibres (CFRP) and glass fibres (GFRP). The fibres can be arranged unidirectionally or most frequently in the form of 2D woven fabric or for special applications in the form of 3D woven fabric. The unidirectional reinforcement possesses the best utilisation of fibres when uniaxial external loading in the direction of fibres axes of the composite material is applied. However, the majority of applications suffer by the presence of combined loading (multiaxial) and therefore usually 2D woven fabric is used instead. The employment of 2D woven fabric can ensure ability of the composite material to offer appropriate biaxial (in plane) properties which are, however, lower than properties obtained in the case of uniaxially reinforced composite materials in preferred orientation.[1–7] It is given by lower number of acting fibres compared to the unidirectional composite in each direction when 2D reinforcement is used. Polymer based matrices are used thanks to their good workability, shaping and good ratio between price and properties. The main disadvantage can be seen in the low resistance to high temperatures of such matrix given by the polymer glass transition temperature and partially also by the fibres used and the environment influence. The glass transition temperature is for most of used polymers between 65 and 120 °C. However, the application temperature of FRP composites can be higher in some cases but it should not exceed temperature between 200 and 300 °C for long exposition time.[8,9] The limiting part of FRP composites is the polymeric matrix. On the other hand the ceramic matrix composites (CMCs) reinforced by long fibres are able to sustain long term exposition to temperatures above 1000 °C together with higher strength and stiffness. The weak point of CMCs is their low fracture resistance and many times higher production price given partly by expensive raw materials

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and by energy demanding processing. The CMCs reinforced by the long fibres are predominantly used in advanced applications for highly loaded parts in the airspace, military and chemical industry. The gap between cheap, reliable FRPs and expensive, brittle CMCs can be filled by hybrid composites. Many authors try to bring advantages from the polymeric and ceramic world together. SiOC glass prepared by the pyrolysis (thermochemical decomposition) of polysiloxane based resins possesses excellent thermal stability at temperatures up to 1500 °C.[10–16] The SiOC based glasses can be modified by changing of chemistry of precursors allowing preparation of composites where no fibre treatment such as a coating is necessary. This fact simplifies the processing of the composite significantly.[17–20] Other possible way of adjusting the interface bonding between matrix and fibres is application of partial pyrolysis where polymeric chains are not completely transformed to the fully amorphous SiOC glass as was reported elsewhere.[21–26] The material prepared by the partial pyrolysis has limited temperature of application which is close to the temperature of the pyrolysis. Therefore the application of high temperature resistance ceramic fibres (e.g. Nextel 720) is not worthwhile and usage of basalt fibres seems to be more effective solution.[27,28] The advantage of the basalt fibres application is their availability and low price comparing to the ceramic fibres. Additionally, it was proved in previous works that by the application of the partial pyrolysis of polysiloxane resins high fracture resistance, appropriate strength and good thermal stability controlled by properties of the fibres and degree of transformation during the pyrolysis can be achieved. The good fracture resistance can be achieved only when effective toughening mechanisms take place during the fracture process. A number of toughening mechanisms is known (i.e. crack bridging, crack deflection, fibre pull-out, micro-cracking shielding, delamination etc.), however, only their optimal combination can lead to the expected result.[29–31] The fibre matrix interface plays the key role determining how effective the given mechanism will be. When mainly fibre pull-out is acting, the fracture toughness can be significantly increased in the case of unidirectional fibre reinforced ceramic composites. This study uses two kinds of commercially available resins to demonstrate influence of the matrix precursor and the basalt 2D woven fabric with the orientation 0°/90°. The effect of the partial pyrolysis on the resulting properties determined at static and dynamic loading will be expressed. Also results from the fractographic analysis will be discussed in detail.

2. Materials and methods

Two polymeric precursors based on siloxane for a composite matrix were selected, i.e. polymethylsiloxane resin – MS (Lukosil M130) and polymethylphenylsiloxane resin – MPS (Lukosil 901) both produced by Lučební závody Kolín, Czech Republic. The partial polymer-to-ceramic thermochemical transformation was done by the pyrolysis within the temperature range between 600 °C and 800 °C with the step of 50 °C. The basalt plain woven fabric having area weight of 186 g m^{-2}, thread count ratio (warp/weft) of 100/75 produced by VÚLV, spol. s.r.o. Czech Republic was used as a reinforcement. Measured parameters of the basalt roving used for the manufacturing of the fabric were following: the linear mass density 110 tex, filament diameter range from 9 to 12 microns, density of the basalt fibre equal to 2.72 g cm^{-3}. Tensile strength on the level of 1870 MPa and elastic modulus in tension of 85 GPa were reported by the manufacturer in the material data sheet. The basalt fibres cannot be used at the maximal application temperature mentioned by manufacturer (i.e. 1000 °C) because a significant degradation (softening) of the fibres even below this limit temperature was previously found.[32] However, for the temperature range used for partial pyrolysis in this investigation mentioned fibres are suitable. Application of two matrix precursors (MS and MPS) led to manufacturing of two sets of composite materials further mentioned as MSC and MPSC. First, the fabric was impregnated with the resin diluted by solvent and then was dried at room temperature. Then the composite plates were manufactured by lamination of manually prepared prepregs. Sixteen layers of prepregs were stacked in the same orientation, by warp, in the longitudinal direction of the mould. Curing was carried out under pressure in a heated mould with controlled temperature and pressure up to 250 °C. During release of the reaction water at the temperature range of 220–250 °C the maximum pressure of 0.86 MPa was applied. The volume fraction of fibres of the cured composite was approximately 43%. Subsequently, all composites were partially pyrolysed using one of targeted temperatures, i.e. the temperature of 600, 650, 700, 750 or 800 °C, in a protective atmosphere of nitrogen. Composite plates with nominal dimensions of 250 mm × 50 mm × 2.5 mm were prepared and cut into the specimens suitable for mechanical testing. Determination of the static flexural strength and measurement of the Young's modulus was carried out by the testing machine Inspekt 100 (Hegewald&Peschke, Germany). Configuration of the measurement corresponds to the standard.[33] The flexural strength was measured in the three-point bending configuration (span of 40 mm) with an inductive extensometer. All static flexural strength tests were carried out using prismatic specimens with nominal dimensions of 50 mm × 8 mm × 2.5 mm and cross-head speed of 1 mm min^{-1}. Additionally, the information about the consumed energy during fracture process was calculated from the recorded load deflection traces. The calculated energy was taken as an energy (elastic and plastic) up to the point where force drops of 50% of the reached maximum. Determined work of fracture is thereafter mentioned as $WoF_{50\% F_{\max}}$. The 50% drop of the maximal force was selected as a criterion due to the limitation of testing jigs. It was not possible to conduct the test to the total fracture in the most of cases (see Fig. 1). The 50% load drop criterion was selected to allow comparison with the results obtained from the dynamic tests. It is necessary to mention that the consumed energy after this force drop was unknown comparing to the energy consumption during the dynamic loading as will be explained in details in the impact loading section. Further, the normalization of the work of fracture by the sample cross-section allows direct comparison of all obtained values independently on the sample cross-section. For accurate measurement of the Young's and shear modulus in the above mentioned bending samples, a resonant frequency method