COMPETITIVE SIOC COMPOSITES WITH INCREASED THERMAL STABILITY FOR APPLICATIONS IN EXHAUST SYSTEMS

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Abstract
Basalt fiber reinforced SiOC composites for intermediate service temperatures have been developed using state of the art manufacturing technologies approved in the polymer composite manufacturing in combination with metal-organic polymers. After pyrolysis and optional densification cycles, the composites offer excellent thermal stability up to 650 °C, combined with superior tribological properties. Non-flammability and structural stability, up to over 1000 °C, enable applications in hot gas systems and heat shielding. The inexpensive raw material base and the polymeric processing technologies allowing this lightweight material to be fitted in series applications. Beside the mechanical characterization of the composites at room temperature after manufacturing and after thermal aging, porosity and residual properties before and after fire testing were determined. Another focus of research was investigated in the field of tribological optimization of the composite and adjustment of hardness and wear, qualifying the material as a promising candidate to replace traditional friction materials.

1. Introduction

Polymer Matrix Composites (PMC) are widely used in lightweight engineering applications due to their excellent mechanical properties in combination with low density. The manufacturing technologies are fully developed and raw materials are cheap. The major drawback of these reinforced polymers is the limited service temperatures and poor tribological properties. Even with relatively expensive high temperature matrix polymers, like cyanate ester or polyetheretherketone (PEEK), service temperatures are limited below 400 °C. Similar problems can be detected for traditional lightweight engineering materials like light metals. E.g. Aluminum significantly starts to soften at temperatures above 300-400 °C. At the other end of the spectrum of composite materials, Ceramic Matrix Composites (CMC) are located, which can be used for applications up to over 1800 °C. CMC with silicon carbide matrix have been developed by various processing methods, i.e. reaction bonding, CVD/CVI and liquid phase impregnation. This class of composites enables decent mechanical properties also at very high temperatures and provides superior tribological properties due to high hardness and adjustable coefficients of friction. CMC are handicapped by the high cost of processing, energy and investment [1]. Additional interface coatings and high cost raw materials, especially the required ceramic fibers, reduce their field of applications to astronautics and military aviation. For series applications, there is a need for a competitive lightweight material with decent mechanical properties for applications in a temperature range in-between 300 °C up to 1000 °C, where polymer composites are not working anymore, CMC however are far too expensive. The driving force for such a need is seen in weight reduction of passenger cars in order to increase performance and efficiency. A promising material alternative for this intermediate temperature range can be manufactured from metal-organic precursors. Polymer derived ceramics are manufactured out of silicon containing polymers which are thermally transformed into a (glassy) ceramic. These precursors allow the application of manufacturing technologies developed for polymer processing, e.g. injection moulding, filament winding or pressing techniques. A major problem of the transformation from polymer to ceramic is referred to the high mass and volume shrinkage, which leads to significant residual stresses and porosity. [2] Therefore, near-net-shape-manufacturing of bulk ceramics is very difficult. Inert and active filler materials can reduce thus problems. E.g., fiber reinforcement is an option. In the wide field of different silicon precursors, the polysiloxanes maybe applied, due to their commercial availability, oxidation stability and low price. After crosslinking, the siloxane-PMC is pyrolysed to an amorphous SiOC ceramic. In [3], carbon fiber reinforced SiOC composites were manufactured by dry filament winding and vacuum infiltration and properties were investigated. Carbon fibers, either with sizing or desized, offer a suboptimal interface with the brittle SiOC matrix, and thus don’t lead to the intended quasi-ductility, hence mechanical properties are inadequate. Fiber coatings can optimize that issue to create a minimum of ductility. A multilayer coating with a thin carbon layer allowing to slide, followed by a thin ceramic layer increasing the oxidation stability, for use in oxidative atmosphere, enables optimal properties. [4] Fiber coatings can be applied via expensive vapor deposition or via competitive liquid phase impregnation. Nevertheless, coating processes are relatively slow and therefore uninteresting for series applications. In [5,6], the use of natural basalt fibers as reinforcement for polysiloxanes was investigated, producing unidirectional specimens via filament wet winding with very good mechanical properties. Further investigations [7] suggest a positive influence of the high iron oxide content of the basalt fiber on weak interface development to the SiOC matrix, which promotes fiber pull-out without the need of fiber coating. Basalt fibers as reinforcement for mechanically and tribologically charged intermediate temperature composites are a very interesting option, due to the decent mechanical and thermo physical properties in combination with a very attractive price rate. The aim of this project is to develop a manufacturing technology for complex formed, thin walled composite structures in industrial scale and quality. The Resin Transfer Moulding process (RTM) is an ideal technique for high-quality composite parts in small series scale. The process and raw materials were adapted and modified [8] to manufacture polymeric siloxane-preforms with subsequent pyrolysis.

2. Experimental procedure

In this study Basalt fiber reinforced SiOC-composites were manufactured via Resin-Transfer-Moulding and filament winding of metal-organic precursors with following pyrolysis. After crosslinking, the pyrolysis is performed at different temperatures between 700 and 1000 °C under nitrogen atmosphere in steps of 50 K to evaluate the influence of the pyrolysis temperature. Beside a evaluation of mechanical properties according to DIN 658 on a universal testing machine (Zwick, Germany), the tribological behavior of the manufactured composites was analysed with an pin-on-disc tribometer according to DIN 50324 and volume of wear was detected with a perthometer (Mahr, Germany), showing excellent properties in tribology combined with decent mechanical properties. Furthermore, the thermal stability and fire protection performance were evaluated. The flame proofing behavior of the composites in comparison to different comparable polymeric composites was evaluated according to DIN 54837 and ISO 11925-2 detecting flammability, smoke emission and drip-off of samples plates which are flame treated by a propane burner. A surface of a polished SiOC specimen after pyrolysis is shown in Fig. 1. The reinforcement structure of the basalt fabric is clearly visible.

Figure 1. Reflections of a screw on a polished SiOC composite surface with reinforcement structure

3. Results

The evaluation of the fire performance of the SiOC composites against common polymeric composite materials was performed according to German and international standards for rail transportation. The reference composite materials were standard composite materials used in public transportation and lightweight applications. Figure 2 is showing a comparison of the Basalt-SiOC composite (right) with an E-glass fiber reinforced polyester sample manufactured via sheet-moulding-compounding (SMC) which is used e.g. as interior paneling in public transportation (left) and a HT-carbon fiber reinforced epoxy (180 °C system in the middle) after one minute of flame treatment on the edge of the sample plates. The SMC sample rapidly starts burning under release of smoke and heat and a complete loss of cohesion. The same can be detected for the epoxy sample already after a short flame exposure. The Basalt fiber reinforced SiOC composite withstands the flame without burning or release of smoke or heat, due to its inorganic matrix. The structural integrity remains also after a long time exposure of 15 minutes under these conditions with adequate residual strength.

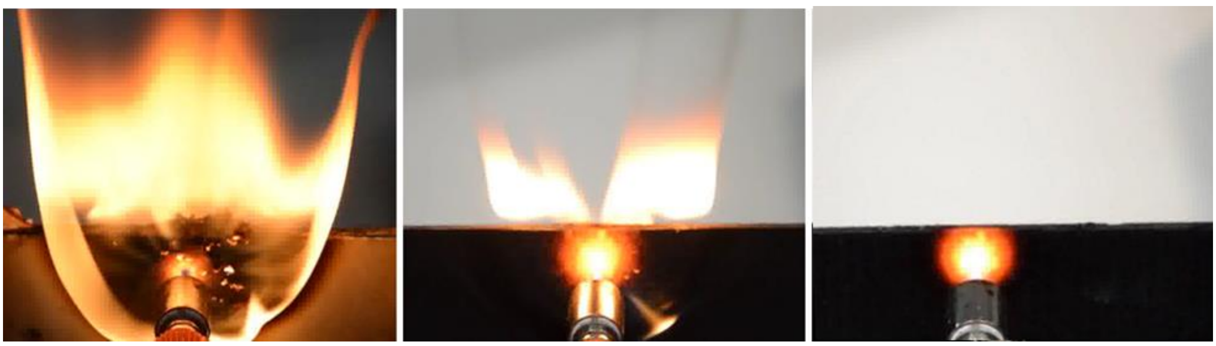

Figure 2. Comparison of E-glass SMC (left), HT-Carbon epoxy (middle) and Basalt-SiOC (right) in burner test

Figure 3 is showing thermo graphic pictures of the backside of the tested materials at the same moment as above. The maximum temperatures are in the same range (645-667,1 °C) for all three samples, much lower than the flame temperature (1200 °C). The heat release of the polyester (left) and the epoxy (middle) sample can be seen. Also the relatively focused heat spot of the SiOC sample (right) due to the low heat conductivity is clearly visible.

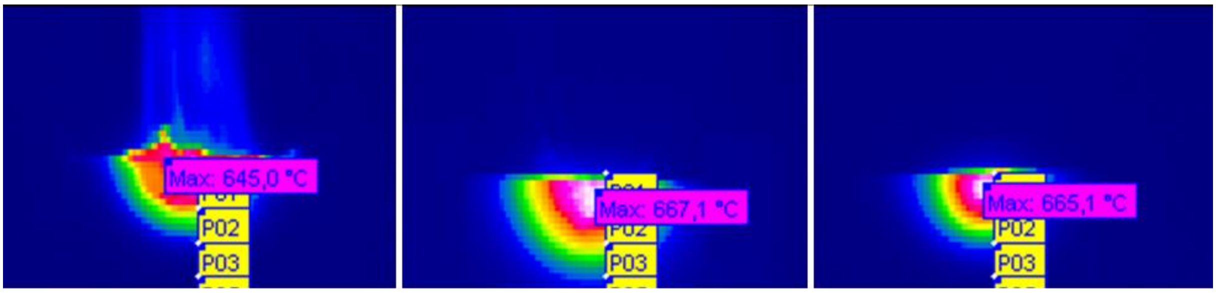

Figure 3. Thermography of the backside of the sample plates from figure 2

After the promising results in laboratory, prototype components for testing in hot gas leading systems, heat shieldings and thermally charged structures were manufactured and have successfully been tested in field tests. Composite exhaust mufflers for motorcycles were manufactured via RTM and filament winding with a weight saving of about 68 % in comparison to the stainless steel standard component. After a full racing distance (400 km), the mufflers were still running without any problem or damage. So the thermo-mechanical stability has been proved sufficient for this case of application. Similar tests were performed with heat shieldings in GT-Racing, showing enough strength and ductility also at service temperatures well above 500 °C to match the requirements.

4. Summary and Conclusion

In this study, Basalt fiber reinforced SiOC hybrid composites were manufactured from polysiloxanes by adapted resin-transfer-moulding- and filament-winding-processes with a subsequent pyrolysis for applications in exhaust systems and heat shieldings. The adaptation of state-of-the-art manufacturing technologies in combination with inexpensive raw materials and comparably low transformation temperatures enables their use for many applications also in series production were standard composites are overcharged due to their limited hardness and heat resistance. The produced composites show interesting properties in the fields of tribology and fire protection. Decent mechanical properties and high COF combined with low wear rates open these intermediate temperature composites interesting possibilities as substitution materials for C/SiC or CFC in industrial use. Novel mineral fiber compositions are tested at the moment, enabling significant higher temperatures in processing and service compared to commercial Basalt fibers. Thermally loaded parts for the use in exhaust systems and heat shielding have been developed and are running in prototype state with promising results. These results will be validated in laboratory evaluations.

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