New approach to design of ceramic/polymer material compounds

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Abstract. The damage tolerance of carbon fibre-reinforced ceramic-matrix composite materials depends on their porosity and can be rather significant. Complex structures are difficult to produce. The integration of simple geometric structures of ceramic-matrix composite materials in complex polymer-based hybrid structures is a possible approach of realising those structures. These hybrid material compounds, produced in a cost-efficient way, combine the different advantages of the individual components in one hybrid material compound. In addition the individual parts can be designed to fit a specific application and the resulting forces. All these different advantages result in a significant reduction of not only the production costs and the production time, but also opens up new areas of application, such as the large-scale production of wear-resistant and chemically inert, energy dampening components for reactors or in areas of medicine. The low wettability of the ceramic component however is a disadvantage of this approach. During the course of this contribution, different C/C composite materials with a specific porosity were produced, while adjusting the resin/hardening agent-ratio, as well as the processing parameters. After the production, different penetration tests were conducted with a polymer component. The final part of the article is comprised of the microstructural analysis and the explanation of the mechanical relationships.

1. Introduction

Carbon fibre-reinforced Carbon Composites (C/C) show great mechanical dampening behaviour, as is the case for ethylene vinyl acetate. This opens up new areas of application for these composites. Examples are energy absorbers for mechanically oscillating or impact related tensions and loads, for example areas of personal protection as a shielding component for projectiles or in an industrial environment as a dampening aid for oscillating masses [1, 2].

The ceramic based compounds currently utilised are characterised by a low energy absorption capacity in relation to their weight and an elaborate production. As a result of this, a new material concept of these compounds is required. There are already a high number of concepts based on metal components e.g. hybrid laminates. These compounds can be composed of one or preferably of multiple energy dissipating components, depending on the place of application and the type of stress placed upon the parts [1–3].

The Improvement of ceramic and polymeric composite materials to create hybrid material compounds enables the utilisation of the beneficial energy dissipating properties of the individual components in an integrated material system. These new materials open up new areas of application, for example as wear and tear resistant and chemically inert energy absorbing parts for reactors or in areas of medical engineering [1, 4].
In order to improve the penetration properties, the surface structure has to be enhanced. During this study, various C/C composites were produced with different resin/hardening agent ratios and the microstructural and mechanical properties were analysed. The investigations were preferably performed by means of 3-point bending tests and the dynamic mechanic thermal analyses (DMTA). Finally, additional penetration tests were conducted on selected polymers. These were carried out in order to give an outlook on further developments regarding hybrid ceramic/polymeric material compounds.

2. Experimental

2.1. Production of the carbon fibre reinforced composites

The C/C composites were produced by means of a multi-levelled process. During the first stage a multi-layered fibre/plastic composite (VF $\approx$ 60 Vol.-%), consisting of twelve layers of fibre fabrics and a phenolic Novolake resin (pre-polymer) each, was created by hand laminating. The plain weave carbon fibre fabric type Aero (style 447), 160 g/m² consists of warp threads and wefts of fibres of the type Tenax® HTA40 (200 tex), 3 k.

The phenolic novolac pre-polymer Prefere 943990 of Dynea (short: PN 943990) underwent a preliminary examination. During the analysis the material showed indicators of the formation of a porous foam matrix carbon. In the carbon fibre-reinforced plastic (CFRP) state, the polymer shows a low amount of pore-development, while the cross-linking in an autoclave at a pressure of > 10 bar can be characterised as medium. The chemical cross-linked agent chosen for the phenolic novolac pre-polymer is called 1,3,5,7- Tetraazatrizyclo[3,3,1,13,7]decane (colloquial: Urotropine). This hardener was selected due to the excellent development of open pores and was added to the PN 943990 in various weight amounts.

After the production of the laminates, they underwent a hardening process in an autoclave (type 4575, Parr Instruments). The temperature for the curing process was determined empirically and is calculated following the formula: $P \{T(t) [°C]| dT(t) [K/min]| t [min]\}i=1$ to 3; $T_\infty$. The empiric set of parameters was determined to be the following: $T_0 = 20 °C; \{80|1|60\}; \{120|1|60\}; \{160|1|60\}; T_\infty = T_0$. The pressure parameters and resin/hardening agent ratios are shown in Table 1.

| No. | resin content [wt%] | Hardening agent content [wt%] | pressure [$10^5$ Pa] |
|-----|---------------------|-----------------------------|---------------------|
| 1   | 96                  | 4                           | 10                  |
| 2   | 96                  | 4                           | 30                  |
| 3   | 88                  | 12                          | 10                  |
| 4   | 88                  | 12                          | 30                  |

In order to enable a complete curing reaction, the samples underwent a hardening and tempering process in a furnace at 320 °C for 4 hours and subsequently cooled freely. Prior to the pyrolysis a separation tool of the type Discotom-6 (Struers) was instructed to cut the CFRP samples. The individual sizes of the samples are discussed further in the chapter about the characterisation.

The second stage of the C/C-composite production consisted of a pyrolysis of the CFRP samples in an argon-filled tube furnace, type CTF 12/65 (Ströhlein). The whole process and program of the pyrolysis was determined and optimised during prior tests. During these tests the thermogravimetric mass degradation of matrix polymers and the thickness of the samples were examined. The whole process was separated in three temperature-time-regimes over 40 h at 300 °C and 1000 °C. Further details of the process will not be disclosed.
2.2. Process supporting examinations
The open porosity of the C/C and CFRP composites was determined according to DIN EN 1389 version B [5].

2.3. Examination of the mechanical characteristics of the C/C composites
The characterisation of the mechanical properties of the C/C-samples was carried out by a three point bending test (Fa. Kammrath & Weiss) according to DIN EN 658-3. The distance between the supporting pins was 40 mm and 9 mm between the loading pins. The testing speed was set to 2 µm/s. Five samples of each sample series were tested [6]. In addition, the mechanical dampening characteristics of the C/C samples were determined by utilising a dynamic mechanical thermal analysis (DMTA) according to DIN EN ISO 6721-1 [7].

2.4. Wetting testing of the C/C composites with ethylene vinyl acetate
The EVA (Ethylenvinylacetat) shows an excellent specific mechanical dissipation factor [8]. For further tests the C/C samples were adjusted for the characterisation methods regarding their size and wetted with EVA. Prior tests showed EVA Greenflex ML 60 (ENI polimeri europa) to be suitable, as the rheological properties are advantageous. The polymer was applied to the C/C composites by means of injection moulding.
The injection pressure was set to 750 bar and the holding pressure to 200 bar. The maximum feed stock temperature was set to 190 °C, while the lowest temperature of the tool was 20 °C. Subsequently the hybrid material compounds were demoulded.

2.5. Analysis of the microstructure
All of the samples were analysed by characterising the cross sections of the C/C composites and the EVA/(C/C) compound materials by utilising an incident light microscope GX51 (Olympus), a camera (Dig 3300) and the image analysis system Stream Motion 1.7.

3. Results

3.1. Results of microstructure analysis

3.1.1. Microstructures of modified CFRP composites
Figure 1 shows the light-microscopic bright field images of the cross sections of the CFRP samples, which were produced from PN 943990, with 4 and 12 % of a hardening agent (HTMA) and varying the hardening pressure from 10 to 30 bar. The samples with less hardener content of 4 % show far more cracks when treated with 10 bar instead of 30 bar ((a) and (b)).
When comparing the samples (a) and (c), which only differ in the content of the hardening agent (4–12 %), one can see that the increase of HTMA content leads to the development of cracks and even the formation of extensive delaminations. A higher pressure during the hardening process decreases the risk of similar structural defects (as can be seen in the comparison of (a) and (b) or (c) and (d)).
3.1.2. Microstructures of C/C composites

Figure 2 shows the light microscopic bright field images of the cross sections of the C/C samples, which were produced from PN 943990, with 4–12 % HTMA and a varying pressure of 10 to 30 bar. The samples with a HTMA content of 4 % and a hardening pressure of 10 bar display more delaminations compared to the samples, which were pressurised under 30 bar ((c) and (d)). The comparison of the samples (a) and (c), which only differ in the increased HTMA content from 4 to 12 %, leads to the same result as it did with the CFRP composites, namely the samples with less hardening agent develop more structural defects than the ones with the lower HTMA content. The samples hardened under a pressure of 30 bar and 12 % HTMA show segmentation cracks (Figure 2c and d). Increasing the HTMA content to 12 % only leads to a decrease of the defects already created in the CFRP state ((c) and (d)).
3.1.3. Microstructures of EVA/(C/C) Interface

Due to the adequately high flexural strength values and above-average mechanical dampening characteristics C/C composites with a hardening content of 12 % and a previously applied pressure of 30 bar, were chosen for wetting tests of the EVA-polymer. A wide interface between the C/C composite and the Polymer can be seen in Figure 3. The image reveals the fact that the segmentation cracks are filled up completely.
3.2. Results of the mechanical tests

3.2.1. Flexural strength of modified C/C composites

Figure 4 displays the average flexural strength values of the various C/C composites and the illustration of the fractures. The images show the development of unilateral shear defects while applying a pressure of 30 bar, whereas a hardening pressure of 10 bar only clarifies a shear fracture on both sides. As a result of these observations the hardening agent content does not seem to have a significant impact. The samples produced with 30 bar yield the higher flexural strength values compared to the other ones. However the best results were achieved by the samples undergoing a pressure of 30 bar and consisting of only 12 % hardening agent. These special samples indicate the generation of micro cracks as a result of the shear force; however these defects are not to be found within the entire sample volume.
3.2.2. Mechanical damping behaviour of modified C/C-composites

The results shown in Figure 5 display the development of a low open porosity and low mechanical damping characteristics of the samples with a low hardening agent content undergoing a treatment with a high hardening pressure. The mechanical damping behaviour is correlating with the behaviour of the open porosity at a hardening content of 4 %. Nevertheless, no significant influence can be shown. However, the samples with the lower content of the hardening agent, namely 4 %, display a significant impact/effect of a change in the pressure exerted upon them on the actual open porosity.
4. Discussion

With the constant hardening pressure of 10 bar the samples consisting of 4% hardening agent showed the highest number of structural defects, such as cracks and delaminations. These are further promoted by the intrinsic gas emission during the cross linking process. Once the pressure is raised to 30 bar, these defects, which are caused by the escaping reaction and decomposition gases, can only be found in the samples with 4% HTMA. The characteristic C/C structural morphology forms within the sample containing 12% of the hardening agent. This fact indicates the existence of a sufficient amount of adhesion between the fibre and the matrix to create reproducible mechanical properties. Due to the production of gases during cross linking reactions, the development of a specific pore-structure is presumable. However, the simultaneous creation of high cohesion forces within the amorphous carbon matrix prevents any delamination processes between the fibre bundles and the matrix. This explains the even development of segmentation cracks, which is a result of the fibres preventing the matrix from any shrinkage. The pre-existing structural defects of the CFRP composites significantly influence the system of the cracks and any delaminations during the pyrolysis. To investigate this further on, additional analyses and examinations of the pore structure are necessary.

The examination of the achieved flexural strength values indicates a connection to the macro structure. Samples containing prior defects displayed lower mechanical strength than their flawless counterparts. During the examination of this connection, an influence of the open porosity, which is accompanied by defects, on the processes was discovered. However, compared to pre-existing data [8] high mechanical dampening values were discovered, which showed an inverse development to the mechanical strength values. The elastic modulus reached the range of thermosetting SMC composite materials, whereas the mechanical dampening equalled the characteristic value of thermoplastic polymers [8]. The infiltration of indentations on the outer boundary surface indicates the possibility of a mechanical adhesion to the C/C composite for the production of hybrid ceramic/polymer material compounds.

**Figure 5.** Mechanical dampening behaviour in depending of open porosity of the C/C composites; effect of open porosity on the mechanical loss coefficient.
5. Summary
In this investigation, porous C/C composites were created by utilising a special carbon precursor. The concentration of the hardening agent was varied between 4 and 12%. During the cross linking reaction a pressure of 10 and 30 bar was applied. These processes were followed by a microstructural characterisation, which was performed by analysing the samples with a light microscope. The C/C composites were further investigated by means of a 3-point bending test and by performing DMTA measurements. Parallel to this process the open porosity was determined. A direct link between the open porosity and the mechanical dampening behaviour was found. The flexural strength correlates with the individually observed structural development during the pyrolysis. In summary the porosity and also the possibility of the development of structural defects increases depending on the concentration of the hardening agent, resulting in a reduction of the flexural strength. The development of a network of cracks suitable for a C/C composite with good mechanical characteristic values and an excellent mechanical dampening is realised with a hardening agent content of 12% and a pressure of 30 bar. The wetting tests show the possibility of a PUR-infiltration of the outer boundary surfaces of C/C composites with a characteristic open porosity.

6. Outlook
The results show the potential of a targeted manipulation of the mechanical dampening behaviour by adjusting the parameters of the wetting process. Further studies and examinations regarding the pore development behaviour of CFRP composites and links to different parameters are necessary. The same thing can be said for the pyrolysis and the parameters attached to that process. Subsequently to these steps the properties of the fibre/matrix interface need to be characterised. In further experiments, the polymer/(C/C) interface is examined in more detail, in order to enable the development of hybrid material compounds from polymer and integrated C/C-based dampening components/elements. Due to the results, which indicate the possibility of a production of selected hybrid ceramic/polymer material compounds, processes and methods of a large-scale production of thermoplastic EVA-like or thermoelastic agents seem to be possible and feasible.

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