Influence of the aluminum die casting process on PEEK layered CFRP in the manufacturing of a hybrid connection

A Marx¹, A Schmid²³, T Haubold², L Pursche², P Schiebel¹ and A Herrmann¹

¹ Faserinstitut Bremen e.V., Am Biologischen Garten 2, 28359 Bremen, Germany
² Fraunhofer-Institut für Fertigungstechnik und Angewandte Materialforschung IFAM, Wiener Str. 12, 28359 Bremen, Germany
³ University of Bremen, Bibliothekstr. 1, 28359 Bremen, Germany

*e-mail: amarx@faserinstitut.de

Abstract. Lightweight design is used as a key technology in a variety of fields to achieve significant weight reduction. Due to its low density in combination with high strength, CFRP and aluminum are predestinated lightweight materials. However, the joining of this material combination is still performed using common technologies like adhesive or mechanical joining. A major challenge at the joining of this material combination is the corrosion behavior. Therefore a novel approach of a hybrid connection between CFRP and aluminum was developed by using the HPDC process of aluminum. During efficient HPDC process, a CFRP structure is recast with aluminum (AlSi10MnMg). To resist the shortly appearing temperature of 700 °C from the liquid aluminum melt, the CFRP is coated with a layer of PEEK. This leads to a material transition, which spatial separates CFRP and aluminum and a hybrid connection with tensile shear strengths up to 22 MPa. Within this work, the influence of the several processing steps on the PEEK layer and the structure of the CFRP was investigated. DSC and TGA results show no significant change on thermal properties of the PEEK. Imaging investigations show the appearance of heat induced volatilizations in the PEEK layer of the hybrid specimens after the HPDC process.

1. Introduction
Lightweight applications are becoming more popular in serval industries, such as the transportation sector as they contribute to emissions reduction [1]. Due to their low weight in combination with high strength, aluminum and carbon fiber reinforced plastics (CFRP) are predestinated lightweight materials. Especially the combination in type of multi-material design enables both materials to be used due to their advantages [2]. However, the joining of this material combination is still accomplished by common joining techniques such as adhesive or mechanical joining [3]. This results in serval disadvantages, for example, extra process times, additional weight caused by the joining elements and a decrease of the strength because of drilling holes in the CFRP structure [4].

To overcome these problems, the focus of research investigations lies on new innovative joining technologies that do not increase the weight of the material combination by adding mechanical joining elements. A common approach is the use of the welding technology, as the partial melting of the thermoplastic results in a connection between the materials [5]. Besides the complex requirements regarding mechanical and thermal properties of the different materials, the occurrence of galvanic corrosion between CFRP and aluminum has to be considered [6]. Within the joining process, actions have to be taken to prevent the development of corrosion.
In this work a novel approach of combining thermoplastic CFRP and aluminum into an intrinsic hybrid composite is investigated. In the primary shaping process of high pressure die casting (HPDC), a CFRP structure is recast with aluminum. Essential for the connection is a decoupling layer, which avoids corrosion and protects the CFRP from high process temperature during the HPDC process. Polyetheretherketon (PEEK) was identified as suitable material due to its stability of high temperatures. In a first approach by [7], hybrid single lap specimens were manufactured with a PEEK layer thickness of 250 µm. It was demonstrated that the tensile shear strength of the hybrid connection increase if quenching and heat treatment is carried out on the specimens after the HPDC process [7]. Within the further development of the hybrid connection, unpublished results show a tensile shear strength up to 22 MPa. Besides single lap specimens, the implementation of CFRP bracket structure into the HPDC of aluminum was shown [8]. A method to describe the failure behavior of the hybrid composite is the use of a cohesive zone model in the finite element method [9].

Therefore, the aim of the presented work is the identification of potential thermal damage in the PEEK layer during the different process steps by the use of differential scanning calorimetry (DSC) and thermogravimetry analysis (TGA). Imaging measurements via computer tomography (CT) and micrographs are carried out to investigate the PEEK layer and the CFRP regarding process induced delaminations and pores.

2. Experimental and material

2.1. Materials

For the manufacturing of the hybrid specimens, the organo sheet Tenax-E TPCL PEEK 4-40-HTA40 consisting of 5 layers carbon fiber fabric [0°/90°|±45°|0°/90°|±45°|0°/90°] with thermoplastic PEEK matrix and a thickness of 1.55 mm was used. To prepare the CFRP structure for the HPDC process, a PEEK coat was applied on the CFRP. Therefore, the PEEK film Victrex aptiv 1000 with a thickness of 250 µm was used.

2.2. PEEK coating

The CFRP organo sheets and the PEEK film were dried for 24 h at 120 °C. The application of the PEEK coating on the organo sheet was executed on a Rucks KV 228 press in an isoforming process, which is optimized for thermoplastic composites. Two separated heated zones allow a fast heating of the composite until the melt temperature of the thermoplastic is reached. A transfer of the mold to the colder zone ensures a defined cooling rate. This characterizes the isoforming process as time and energy efficient [10].

For this work, the organo sheets with PEEK film were placed in a compression tooling and heated up under the pressure of 4.2 bar until thermocouples inside the tooling viewed a temperature of 350 °C. At this temperature, the transfer to the colder zone was carried out and the cooling occurred under the pressure of 4.2 bar. Afterwards the coated specimens were trimmed to their designated dimension of 100 x 40 mm. In this approach, the whole specimens were coated with a PEEK layer. The Process parameters and specimens are shown in Figure 1.
2.3. Aluminum high pressure die casting process

The HPDC process of the aluminum was carried out at the Fraunhofer IFAM on a cold-chamber die casting machine Bühler type SC N/66. The CFRP specimens were dried for 24 h at 120 °C. The aluminum alloy Silafont 36 (AlSi10MnMg) was used. During the HPDC process, the aluminum melt had a temperature of 700 °C and was pressed with a piston speed of 2.35 m/s and a hold pressure of 1000 bar into the 150 °C hot mold. The closing time of the mold was 10 s. An aluminum body with a length of 100 mm, a width of 40 mm and a thickness of 10 mm was casted and simultaneously joined to the CFRP in an overlap area of 40 x 40 mm. Immediately after the HPDC process the hybrid specimens were quenched in water (temperature 20-30 °C). a heat treatment, inspired by T5 treatment for metals, was carried out at 190 °C for 2 h. A manufactured single lap hybrid specimen is shown in Figure 2.

2.4. Analysis methods

Thermally analysis with DSC and TGA were carried out to investigate the thermal influence on the PEEK interface layer during the different process steps and to identify potential thermal damage. The TGA determines the weight loss of the PEEK over a range of temperature to predict the thermal stability and to gain information about the thermal decomposition and degradation behavior [11]. The TGA measurements were carried out with a Q5000 from TA Instruments with a temperature range from 25 °C to 800 °C and a heating rate of 10 K/min in nitrogen and ambient atmosphere. The samples for the TGA were prepared out of the PEEK layer with scalpel and had a weight between 3 and 6 mg.
DSC analysis reveal the melting temperature and enthalpy of fusion of the PEEK, which leads to the degree of crystallinity. According to [12], the thermal history of PEEK causes an impact on the crystal structure. The DSC tests were performed at a DSC Discovery 250 from TA Instruments with a heating rate of 10 K/min and nitrogen atmosphere. The samples for the DSC analysis after the HPDC process were prepared from the middle of the fractural interface of the CFRP side after tensile shear tests. Therefore, they do not represent a direct contact between PEEK and aluminum melt. The sample weight was between 6 and 7 mg.

The process induced delaminations and pores in the CFRP laminate and PEEK layer were investigated by CT scans on a GE Phoenix v/tome/x m with a 240 kV tube, micrographs of the cross section and pictures of the fractural surface in the interface after adhesive failure at tensile shear tests.

3. Results and discussion

3.1. DSC

The used PEEK film Victrex aptiv 1000 reveals an enthalpy of fusion of 40.9 J/g and a melting temperature of 342.1 °C. According to [12], the enthalpy of fusion from complete crystalline PEEK is 130 J/g. This results in a degree of crystallinity of 31.5%. After the application of the PEEK film via isofoming process, the degree of crystallinity increases to 34.1%. According to [10] the degree of crystallinity of the PEEK is effected by the cooling rate. The slower the cooling rate, the higher the degree of crystallinity. The slow cooling rate in the isofoming process could lead to an increase of the crystallinity of 3% compared to the initial PEEK film. After the HPDC process with a high cooling rate, the determined degree of crystallinity decreased to 29.8%. An explanation for the lower degree of crystallinity after HPDC process is the performed quenching and heat treatment. A heating above the glass transition temperature leads to a crystallization of the PEEK [13]. However the annealing temperature of 190 °C was not high enough to lead to a higher degree of crystallinity [14]. According to [15] the properties of PEEK are highly dependent on the degree of crystallinity. A low degree of crystallinity decreases the mechanical properties of PEEK [16]. Hence, as there is no significant difference between the degree of crystallinity in the initial PEEK film and the PEEK after the HPDC process, it can be assumed that no major change in the properties of the PEEK occurred. The determined melting temperatures of the PEEK slightly decreases over the different process steps from 342.1 °C to 340.7 °C. The results are shown in Table 1.

| Process step   | Melting Temperature (°C) | Enthalpy of fusion (J/g) | Degree of Crystallinity (%) |
|---------------|--------------------------|--------------------------|-----------------------------|
| Initial film  | 342.1                    | 40.9                     | 31.5                        |
| After application | 341.9                   | 44.4                     | 34.1                        |
| After HPDC    | 340.7                    | 38.7                     | 29.8                        |

The graphs of the DSC analysis are shown in Figure 3. All specimens show a similar heat flow behavior at the glass transition temperature and melting temperature. Since the curves are very similar, no indication of a thermal damage caused by the short contact time with the 700 °C aluminum melt is visible. The thermal properties of the PEEK remain unchanged during the different process steps. Since the mechanical properties of PEEK rise with an increasing crystallinity, a heat treatment adapted to PEEK should be investigated to increase the mechanical properties of the hybrid connection [14].

Since the DSC analysis identified no thermal damage on the PEEK, additional investigation such as X-ray photoelectron spectroscopy (XPS) and infrared spectroscopy (IR) are recommended to determine changes of PEEK direct at the joining zone with the aluminum.
3.2. TGA

The decomposition of PEEK is described in two steps. During the first decomposition step a random chain scissions of ether and ketone occur and result in a fast and rapid weight loss of about 45% of the mass, followed by a second step with a slower decomposition, in which under air almost the whole mass is volatized [17].

The start of thermal decomposition of the initial PEEK film Victrex aptiv 1000 was identified at about 530 °C under ambient atmosphere and 550 °C under nitrogen atmosphere see Figure 4. A rapid weight loss occurs until 600 °C. As described by [17] the decomposition under nitrogen and ambient atmosphere differs in the second step. Compared to the initial PEEK film, the decomposition of the PEEK, after the HPDC process, starts at 470 °C under ambient atmosphere and 540 °C under nitrogen atmosphere. Except for the difference in the initiation of the decomposition, the behavior under nitrogen is very similar for both specimens. Under ambient atmosphere, the decomposition of PEEK after the HPDC occurs at slightly lower temperatures.

Investigations from [15] show a similar behavior of thermally stressed PEEK at wear testing. A faster decomposition of PEEK occurs, because of the damage of linear chain segments and the reduction of active sides for pyrolyti reaction. The weight loss in the first decomposition step indicates the quantity of the decomposition of the linear structure inside the PEEK [15]. Due to the fact, that just small differences in the decomposition behavior of the PEEK specimens appears, it can be assumed that a slight decomposition occurred during the HPDC process.

A TGA of the PEEK layer after the application in the isoforming process was renounced, because the process temperatures of 350 °C are below the investigated decomposition temperatures of PEEK.
Figure 4. TGA analysis of the PEEK layer at a heating rate of 10 K/min under ambient and nitrogen atmosphere.

3.3. Micrographs

To investigate the quality of the PEEK coated CFRP specimens, micrographs of the cross sectional area were prepared, see Figure 5. The coated PEEK film is homogenously bonded with the PEEK matrix of the organo sheet. The thickness of the resulting PEEK layer was measured on the micrographs and reveal an average PEEK coating thickness of 294 µm. Furthermore, the micrographs indicate the appearance of single pores inside the CFRP. Due to the fact, that processing temperature at the PEEK coating were below the investigated decomposition temperature, volatilization on the basis of decomposition gases is excluded.

Figure 5. Micrograph in the cross sectional area of the PEEK coated CFRP before the HPDC process.

3.4. CT Scans

Micrographs just display a single section of a specimen, therefore CT scans were conducted to investigate imperfection like pores and delamination in the whole CFRP specimen. The CT scan, shown in Figure 6, displays partial single pores inside the CFRP after the PEEK coating in the isoforming process. The results agree with the investigated pores in the micrograph.
To show the influence of the HPDC process on the structural integrity of the PEEK coated CFRP, the same specimen as shown in Figure 6 was investigated after the HPDC process and heat treatment. Therefore, the interface area between the PEEK coated CFRP and aluminum was investigated, shown in Figure 7. It becomes obvious, that massive pores occur in the PEEK interface between aluminum and CFRP. Besides the interface no pores or delamination are visible in the CFRP. During the HPDC process the PEEK layer is for a low time span exposed to the melted aluminum with a temperature of 700 °C. According to [18] the volatile decomposition products of PEEK in this temperature range are phenol, benzene, CO and CO₂. The CT scans indicate that a volatilization of these gas components in consequence of the heat during the HPDC process occurred in the interface.

3.5. Fractural surface analysis
Conducted mechanical test reveal a tensile shear strength of 15.6 MPa, related to the casted area of 1,600 mm², for the presented series of hybrid specimens. A picture of the fractural surface area is shown in Figure 8. A mainly adhesive failure occurs between the PEEK interface and the aluminum, with thin remains of PEEK on the aluminum surface. The occurring pores are a consequence of the volatilization of gas products during decomposition in the PEEK interface. The specimen shows the biggest pores in the middle, the area assumed to achieve the highest thermal input during the HPDC process. A black value analysis reveals that 38 % of the surface form the PEEK interface consists of pores. The occurring pores reduces the connection surface and thus the strength of the connection. Nevertheless, tensile shear test of specimens without PEEK coating show a strength of just 6.4 MPa. Despite the pores, the spatial separation between the CFRP and aluminum through the PEEK layer is visible and indicates no direct contact between the CFRP and aluminum. Hybrid specimens with different HPDC process parameters and heat treatments achieve tensile shear strengths up to 22 MPa and show smaller pores in the fractural surface area.
Figure 8. Fracture surface of the single lap hybrid specimen with adhesive failure after tensile shear tests, a) CFRP side with the PEEK interface, b) aluminum side.

4. Conclusion
In the presented work, the TGA and DSC analysis reveal no significant thermal degradation within the investigated PEEK layer due to the HPDC process. However, the imaging investigation showed pores in the interface which are affiliated to the volatilization of the PEEK due to the high temperatures of the HPDC process. Further research needs to be conducted to investigate the interface between PEEK and aluminum with chemical analysis such as XPS or IR. The determined degree of crystallinity inside the PEEK layer is slightly lower than in the initial PEEK film. A more suitable PEEK annealing treatment of the hybrid specimens could increase the degree of crystallinity and strength.

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References
[1] Friedrich H E 2013 *Leichtbau in der Fahrzeugtechnik* ed H E Friedrich (Wiesbaden: Springer Fachmedien Wiesbaden)
[2] Kroll L and Nestler D 2019 Verbundwerkstoffe und Werkstoffverbunde *Technologiefusion für multifunktionale Leichtbaustrukturen* ed L Kroll (Berlin: Springer Vieweg) pp 11–22
[3] Zhang D, Zhang Q, Fan X and Zhao S 2019 Review on Joining Process of Carbon Fiber-reinforced Polymer and Metal: Applications and Outlook Xiyou Jinshu Cailiao Yu Gongcheng/Rare Met. Mater. Eng. 48 44–54
[4] Amancio-Filho S T and Blaga L A 2018 *Joining of polymer-metal hybrid structures: Principles and applications* ed S T Amancio-Filho and L-A Blaga (JohnWiley & Sons)
[5] Pramanik A, Basak A K, Dong Y, Sarker P K, Uddin M S, Littlefair G, Dixit A R and Chattopadhyaya S 2017 Joining of carbon fibre reinforced polymer (CFRP) composites and aluminium alloys – A review Compos. Part A Appl. Sci. Manuf. 101 1–29
[6] Wu X, Sun J, Wang J, Jiang Y and Li J 2019 Investigation on galvanic corrosion behaviors of CFRPs and aluminium alloys systems for automotive applications Mater. Corros. 70 1036–43
[7] Schmid A, Arnaut K, Clausen J, Koerd M, Struss A, Wöstmann F J and Busse M 2017 Intrinsic aluminum CFRP hybrid composites produced in high pressure die casting with polymer based decoupling layer Key Eng. Mater. 742 KEM 197–204
[8] Schmid A, Arnaut K, Clausen J, Koerdt M, Struß A, Woestmann F-J and Busse M 2018 Process concepts for the manufacturing of hybrid composites made from aluminum and CFRP with a polymer-based decoupling layer. *Int. Konf. Hybrid Mater. Struct. 2018. Proc.* 216–22

[9] Struß A, Schmid A, Ebrahimi A, Jablonski F and Busse M 2020 Description of the Boundary Layer Behavior of an Aluminum–Carbon-Fiber-Reinforced Polymer Hybrid Compound Using a Cohesive Zone Model. *J. Fail. Anal. Prev.* 20 930–5

[10] Koerdt M 2020 *Development and analysis of the processing of hybrid textiles into endless-fibre-reinforced thermoplastic composites* (Universität Bremen)

[11] Day M, Cooney J D and Wiles D M 1989 The thermal stability of poly(aryl-ether–ether-ketone) as assessed by thermogravimetry. *J. Appl. Polym. Sci.* 38 323–37

[12] Wu Z, Zheng Y Bin, Yu H X, Seki M and Yosomiya R 1988 Effect of thermal history on crystallization behavior of polyetheretherketone studied by differential scanning calorimetry. *Die Angew. Makromol. Chemie* 164 21–34

[13] Cebe P 1988 Annealing study of poly(etheretherketone). *J. Mater. Sci.* 23 3721–31

[14] Regis M, Bellare A, Pascolini T and Bracco P 2017 Characterization of thermally annealed PEEK and CFR-PEEK composites: Structure–properties relationships. *Polym. Degrad. Stab.* 136 121–30

[15] Zhang M Q, Lu Z P and Friedrich K 1997 Thermal analysis of the wear debris of polyetheretherketone. *Tribol. Int.* 30 103–11

[16] Gao S L and Kim J K 2002 Correlation among crystalline morphology of PEEK, interface bond strength, and in-plane mechanical properties of carbon/PEEK composites. *J. Appl. Polym. Sci.* 84 1155–67

[17] Patel P, Hull T R, McCabe R W, Flath D, Grasmeder J and Percy M 2010 Mechanism of thermal decomposition of poly(ether ether ketone) (PEEK) from a review of decomposition studies. *Polym. Degrad. Stab.* 95 709–18

[18] Tsai C J, Perng L H and Ling Y C 1997 A study of thermal degradation of poly(aryl-ether-ether-ketone) using stepwise pyrolysis/gas chromatography/mass spectrometry. *Rapid Commun. Mass Spectrom.* 11 1987–95