Hybrid casting – An investigation into the interface of high-pressure die-cast intrinsic aluminum-PEEK-CFRP hybrid composites

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Abstract. The joining of plastic-based fiber composites and light metals is increasingly becoming the focus of lightweight construction applications. To date, conventional mechanical and adhesive joining techniques are still the predominant means to produce hybrid composites. The aim of this work was to create a hybrid composite of CFRP and aluminum in a novel way using the economic high-pressure die-casting process without the use of additional joining elements. The casting process implies the direct contact of molten metal (AlSi10MnMg) and thermally resistant polyetheretherketone (PEEK) under short-term temperatures of about 700 °C. The material and process parameters lead to a material transition that spatially separates the CFRP and the aluminum while guaranteeing a firm bond with lap shear strengths up to 22 MPa. The results of the TEM investigations into the boundary region between PEEK and the AlSi10MnMg alloy show that both materials are locally joined without gaps. Furthermore, the chemical EDX, XPS and IR spectroscopy results indicate a tendency for the bond to form through the thermal alteration of the polymer and the associated modification of the bonding possibilities in the direct contact area.

1. Introduction

The optimization of performance and efficiency in the technical field are driving forces for lightweight construction, and the realization of lighter components always underpins the further development of innovation. In addition to the use of alternative materials, the combination of different types of materials within a structure offers great potential for composite and lightweight design [1, 2]. Especially with the increasing use of CFRP, the hybrid joining of light metals and carbon fiber reinforced thermoplastics is a major research focus in the field of joining technology [3, 4].

The joining of different materials has a complex requirement profile. In addition to the compatibility of the mechanical and thermal properties, the electrochemical interaction in the contact area of the joined materials is of particular relevance [5, 6]. Accordingly, there are many potential solutions, with the most established being conventional joining techniques based on mechanical and adhesive bonding. However,
these joining processes have specific disadvantages, such as additional weight input from fasteners or surface pretreatments. [7].

Within the framework of this research, hybrid joints that can be implemented without these limitations represent a major research focus. For example, [8] and [9] described welding techniques, which imply the melting of the fiber composite component’s plastic to join both materials.

In addition, primary forming processes, such as plastic injection molding and light-metal-based high-pressure die-casting, make it possible to reduce the number of production steps when primary forming and joining processes are carried out simultaneously.

[10] showed that it is possible to generate a direct composite consisting of polyetheretherketone (PEEK) based CFRP and aluminum in the high-pressure die-casting process without involving an induced form closure. Hereby, the bond between CFRP and aluminum, with tensile shear strengths of around 16 MPa, is generated mainly by a 250 µm thick PEEK layer, which is applied to the CFRP in the area of the joining surface before the high-pressure die-casting process. PEEK also enables simultaneous electrochemical separation of aluminum and carbon fibers [10]. Within the scope of the further development of the hybrid connection of PEEK and aluminum using the high-pressure die-casting process, lap shear strengths of up to 22 MPa are achieved. By comparison, [11], joining PEEK and the 6061-T6-Al alloy, and [12], with a composite of CF-PEEK and the AA6082-T6-Al alloy, achieved comparable strengths in the range of 20 MPa without additional joining elements or strength-enhancing measures such as surface treatments or structuring.

Meanwhile, [13] and [14] already showed that a direct connection between PEEK and metal without form or force fit is technically feasible. Oxidic compounds that can form a metal-O-C bond appear to be of particular relevance here [15, 16].

The aim of this work is, therefore, to use microscopic (TEM) as well as spectroscopic means (EDX, XPS, IR spectroscopy) to show how a short-term temperature of around 700 °C within the high-pressure die-casting process affects the PEEK, the formation of the interface, and the bonding of PEEK and aluminum in the hybrid compound.

2. Experimental and materials

2.1. Materials

A carbon fiber reinforced PEEK composite laminate (ThermoPlastic Consolidated Laminate, Tenax-E TPCL PEEK HT-A40, Teijin Carbon, Wuppertal, Germany) with a five-layer fabric [0°/90° +/- 45° 0°/90° +/-45° 0°/90°] and the dimensions 100 mm x 40 mm with a thickness of 1.5 mm was used to produce the hybrid composites. In the area of the surface to be joined (40 mm x 40 mm), the CFRP inserts were coated with a 250 µm thick PEEK film (type Aptiv 1000, Victrex plc, Lancashire, UK), as shown in Figure 1. The coating was applied using a hot-pressing process, performed on a Rucks KV 228 press. The process takes place at a maximum temperature of 350 °C and with a consolidation pressure of 4.2 bar (holding time of 20 minutes).

The work was carried out at Faserinstitut Bremen e.V.

An AlSi10MnMg alloy (Silafont 36, Rheinfelden Alloys GmbH & Co. KG, Rheinfelden, Germany) was used for the metal component.
2.2. Composite manufacturing and mechanical testing

Before the casting process, the CFRP components were dried for 24 hours at 120 °C in a circulating air chamber furnace (N250/85 HH, Nabertherm GmbH, Germany), and the joining surfaces were cleaned with acetone directly before pouring.

Using a temperature-resistant adhesive, the CFRP inserts were fixed selectively in the die-casting tool and away from the joining area. Subsequently, the CFRP was partially cast-on with the AlSi10MnMg alloy using a cold-chamber high-pressure die-casting machine (Bühler SC N/66, Bühler AG, Uzwil, Switzerland). Before each casting cycle, the tool was cleaned to remove any residue and coated with the release agent SL 1697 S from Chem-Trend (Chem-Trend GmbH, Maisach, Germany). Relevant process parameters selected were a plunger speed of 2.35 m s$^{-1}$, a melt temperature of 700 °C, an average mold temperature of 150 °C and a holding pressure of 1000 bar (holding time of 10 s). The PEEK-coated CFRP was placed in the mold so that the joining surface was at the furthest point in relation to the gate system. After the hybrid cast structures (Figure 2) were removed from the tool, they were quenched in a water bath at a temperature of 20-30 °C. The samples were stored at room temperature until heat treatment.

The heat treatment was performed in a chamber furnace (N 300/WAX, Nabertherm GmbH, Lilienthal, Germany). The samples were stored in the furnace for two hours at 190 °C, in accordance with a T5 heat treatment.

The high-pressure die-casting experiments took place at Fraunhofer IFAM.

![Figure 2](image_url)  
**Figure 2.** A high-pressure die-cast Al-PEEK-CFRP hybrid composite. The arrow shows the entry point of the melt during the mold-filling.

The single-lap test specimens were tested according to DIN EN ISO 527-4 with a tensile testing machine from Zwick (Z250, ZwickRoell GmbH & Co. KG, Ulm, Germany).

The tests were performed at Faserinstitut Bremen e.V.

2.3. Analysis methods

2.3.1. TEM (transmission electron microscopy) and EDX (energy-dispersive X-ray spectroscopy)

For the structural and elemental investigation of the interface between the Al alloy and PEEK, TEM analysis was carried out using a Tecnai F20 S-TWIN microscope (FEI now Thermo Fisher Scientific, Eindhoven, Netherlands) with a field emission gun operated at 200 kV, resulting in a point resolution of 2.4 Å. TEM images were acquired with a 1k × 1k slow-scan CCD camera embedded in a Gatan GIF2001 image filter. In the interface between Al and PEEK, elemental analysis was performed by means of EDX using the EDAX r-TEM-EDX Detector of the TEM operated in scanning mode (STEM). The EDX detector has an energy-resolution of 136eV measured at Mn-Kα. The STEM images were obtained by a Fischione HAADF-STEM Detector.

The TEM samples were prepared via the well-known focused ion beam (FIB) technique in an FEI Helios 600 dualbeam machine, as described in [17].

The TEM and EDX analyses were performed at Fraunhofer IFAM.
2.3.2. XPS (x-ray photoelectron spectroscopy) and solution test of PEEK. For the XPS analysis, the exposed fracture surface of a mechanically tested sample was used. The measurements were performed in regions, which were characterized by the absence of significant PEEK residues as indicated by a visual inspection using a light microscope (adhesive failure mode). The area of analysis was 0.4 x 0.4 mm. The XPS measurements were performed using a Thermo K-Alpha K1102 system and monochromatized Al K-Alpha irradiation (1486.7 eV). The angles of incidence and emission were 57.4 and 0 ° respectively. Spectra were acquired in Constant Analyser Energy mode (CAE) at 150 eV (survey spectra) and 20 eV (high-resolution spectra). The samples were neutralized using a combination of low-energy electrons and argon ions. The binding energy scale of the spectrometer was calibrated using the main peaks of Cu, Ag and Au. Moreover, the binding energy scale was referenced to the C1s binding energy of surface organic compounds at 285.0 eV. The elemental quantification was performed using instrument specific elemental relative sensitivity factors. The depth of information was around 10 nm.

In order to validate irreversible bond formation, the fractured aluminum surface was extracted in a 1:3 boiling solution of 9-fluorenon and diphenyl ether for 5 min, which represents a good solvent for PEEK at minor concentrations. However, strongly adsorbed PEEK monolayers are not desorbed under these conditions as shown by preliminary experiments on Ti coated Si-wafer (not shown). The XPS analysis and solution experiments were carried out at Fraunhofer IFAM.

2.3.3. IR Spectroscopy (Infrared spectroscopy). The IR measurements were performed on a Hyperion 3000 IR microscope (Bruker Corporation, Massachusetts, USA). The IR spectra were recorded with an ATR objective in emission mode in the range of 600 - 4000 cm⁻¹ and a scan number of 64. The data were then evaluated with the Opus software. The samples were measured on the unaffected pure PEEK foil, on the fracture surface of a composite sample after the tensile shear test as well as in cross section of the interface between aluminum and PEEK. The reference spectrum used was that of pure PEEK.

The IR spectroscopy was performed at Fraunhofer IFAM.

3. Results and discussion

3.1. Mechanical testing

Mechanical testing of the single lap shear specimens resulted in an average lap shear strength of 20.55 ± 0.99 MPa (sample size of five), calculated with a bonding area of 1600 mm². The maximum value was about 22 MPa. Based on these strengths the interface between Al and PEEK was investigated in detail. The typical fracture surfaces and the characteristic failure behavior of the samples are shown in Figure 3.

![Figure 3](image-url)
3.2. TEM

Figure 4 depicts the prepared FIB lamella, and the results of the TEM analysis are present in Figure 5. The images show that there is a gap-free and material-locking connection between the PEEK and the aluminum-based alloy. The atomic plane distances measured within the scope of the measurement accuracy illustrate the local structural differences. In aluminum, the planes show a distance of about 2.1 Å. In the interface between aluminum to PEEK, however, the atomic lattice seems to be widened and locally has a lattice plane distance of about 2.9 Å. The widened lattice structure could indicate an oxide complex formation.

![Figure 4. The prepared FIB lamella from the combination of PEEK and AlSi10MnMg (with tendentially contained silicon phases).](image1)

![Figure 5. An HRTEM image of the connection between AlSi10MnMg and PEEK. The marked sections illustrate the different atomic lattice structures of both the aluminum alloy and the interface between Al and PEEK.](image2)

3.3. EDX

Figure 6 shows the results of the line scan (EDX) of the same sample used in the TEM. Focusing the supposed relevant chemical constituents, it can be seen that in the investigated section of the interface between the AlSi10MnMg alloy and PEEK, the elements magnesium and oxygen are predominantly present, with a local increase in intensity ranging from 8 nm to 11 nm. The superficial precipitation of Mg in Al alloys is known. However, it is not possible to draw specific conclusions on the binding conditions using the EDX analysis procedure. Based on the changes in the atomic lattice structure shown in the TEM analysis, it is assumed that the interface between the AlSi10MnMg alloy and PEEK within the sample could be an oxidic bond. The lattice spacing of 2.9 Å, determined within the scope of the measurement accuracy, is consistent with the results according to [18], which reported an atomic lattice spacing of 2.97 Å in an MgO lattice. In addition, PEEK and metal are clearly separated. This probably indicates adsorption. Based on this, a solution test is carried out below. This allows the detection of irreversibly adsorbed PEEK layers, but also their chemical characterization.

The potential for the formation of metal-polymer complexes in such hybrid composites has been discussed in several publications. [14], for example, showed that a MgCO₃ compound is formed when an AZ31 magnesium alloy is thermally joined with PEEK. [13] dealt with the metallization of PEEK with pure aluminum, aluminum bronze and copper. In the investigation, liquid metal droplets were applied to the plastic, which guaranteed a certain comparability to this work. Using TEM and EDX analyses, the potential presence of copper(I)-oxide copper(II)-oxide as well as copper(II)-hydroxide and copper(I)-oxide were demonstrated.

The work of [19] also supports the hypothesis that complex formations between a metal and a polymer are possible in principle. The authors produced a chemical compound of different materials by
coating aluminum with polyamide. Specifically, an Al-O-C complex was detected by means of XPS analysis, initiated or formed by the cleavage of the carbonyl group (C=O) of the polymer.

![Image of Al-O-C complex detected by XPS analysis](image)

**Figure 6.** The result of a line scan (upper left) in the transition region between PEEK and the aluminum alloy; the measuring range is visible in the STEM image (upper right). The measured intensities (note the scales) of the respective elements are shown in the individual diagrams (below). With reference to the investigated area, the alloying elements manganese and silicon are excluded from the shown result, because of their noisy like progression of element distribution and the low detected concentrations compared to the main present elements.

### 3.4. XPS and solution test of PEEK
The area of the aluminum sided fracture surface of the sample examined by XPS is shown and marked in Figure 7. On the left, the considered area after the lap shear test is shown, on the right the same area after the solution test.

![Image of fracture surface after lap shear test and solution test](image)

**Figure 7.** Area of the fracture surface of the hybrid PEEK-aluminum sample examined in the XPS analysis (white framed). On the left, the surface is visible directly after the lap shear test; on the right, after an additionally performed PEEK solution bath.
The results of the analysis show that directly after the lap shear test, the apparently metal like surface still contained an average between 75.8 and 77.2 At.-% carbon and 18.0 and 18.7 At.-% oxygen, as shown in Table 1. The comparatively high percentage of organic matter indicates that PEEK residues still adhered to the metal within the measuring range.

Table 1. The concentration of the elements detected on the fracture surface, shown in At.-%. The positions represent individual measuring points in the measuring range. The measuring sensitivity was about 0.1 At.-%.

|        | C  | O  | Al | Mg | F  | Na |
|--------|----|----|----|----|----|----|
| Pos.1  | 77.2 | 18.0 | 3.4 | 0.5 | 0.3 | 0.6 |
| Pos.2  | 75.8 | 18.7 | 3.8 | 0.7 | 0.8 | 0.2 |

After the solution bath, the polymer residues still adhering to the fracture surface could be identified analytically. The measured percentage of carbon was between 68.4 and 79.3 At.-% and the percentage of oxygen was between 17.4 and 23.5 At.-%, as shown in Table 2. Analytically, it was still possible to detect significant adhesive residues of PEEK after the solution test. The approach to expose stronger adsorbed polymer layers using adequate solvents, is well established [20; 21]. The parameters and conditions of the solution bath for PEEK were determined empirically. From experiments and experiences with this for metal-to-PEEK bonds tailored method it is also possible to dissolve strong adsorbed polymer chains, which illustrates the efficiency and potential of this approach. The microscopic images (Figure 7) show a notable removal of polymer residues from the surface.

Table 2. The concentration of the elements detected on the fracture surface, shown in At.-%. The positions represent individual measuring points in the measuring range. The measuring sensitivity was about 0.1 At.-%.

|        | C  | O  | Al | Mg | F  | Na |
|--------|----|----|----|----|----|----|
| Pos.1  | 79.3 | 17.4 | 2.4 | 0.4 | 0.3 | 0.1 |
| Pos.2  | 70.4 | 22.7 | 4.8 | 1.3 | 0.4 | 0.1 |
| Pos.3  | 68.4 | 23.5 | 5.3 | 1.5 | 0.7 | 0.1 |

The results show that PEEK is at least partially strongly adsorbed at the interface. This explains the observed high adhesion. The presence of the macroscopic gel residues on the surface also indicates that crosslinking reactions have taken place, which are known to be caused by oxidative degradation of PEEK by e.g. O₂, like also shown in [22]. Consequently, the gel residues bind to the surface and cannot be removed. Overall, the results indicate a multilayer interface structure:

Al | MgO | PEEKadsorbed | PEEK, PEEKGel | PEEK

It has already been shown [23] that 24-hour heat treatments at temperatures above 319 °C can lead to crosslinking in PEEK. The occurrence of these structurally modified molecules was demonstrated by [23] through analogous chemical solution experiments. A possible quantification of the thermally
induced change in PEEK under tribological load as a function of oxygen availability was described in [24], whereby crosslinking processes could be detected within two hours. In general, the interaction and mechanisms behind the stronger adsorption of single polymer layers is complex and especially for the contact of metal melt and PEEK still unknown. The origin of the adhesion could only be suggested, based on combining the results of the different investigation methods. From microscopic analysis a mechanical interlocking can be excluded. Also an interdiffusion of the different materials does not occur and the EDX results show a direct transition of the components. Further assumed the bonding strengths is mainly based on physisorption, such as van der Waals and polar forces. The complexity of metal-to-plastic adhesion is also shown in [25; 26]. While using the Good-Girifalco model [25] to describe the irreversible bonding of polystyrene and aluminium, the thermodynamic consideration is not sufficiently explained. [26] postulate that also the time depended absorption kinetics should be taken into account.

3.5. IR Spectroscopy

Finally, IR spectroscopy was performed to describe the possible process-related influences on the structural properties of PEEK. The results in the form of a comparison of the IR spectra of the unaffected PEEK film (Figure 8, top) and the thermally influenced PEEK in the interface to the metallic casting are shown as an example in Figure 8 (bottom) for the fingerprint range of PEEK up to 1800 cm⁻¹.

The spectra show a change in peak maxima relations as a result of the high-pressure die-casting process. The carbonyl peaks at 1653 cm⁻¹ and 1307 cm⁻¹ were related to the peaks at 1280 cm⁻¹, belonging to the stretching vibrations of the diphenyl ether groups and the phenyl peak at 1490 cm⁻¹.

![Figure 8](image-url)

**Figure 8.** The upper part of the diagram shows bands of the IR spectrum characteristic of non-processed PEEK. The results of the measurement after the high-pressure die-casting process are presented in the lower part of the diagram (dashed lines) and superimposed with the measurement of the upper part of the diagram of non-processed PEEK (continuous line). The arrows show how the peaks of the two spectra rise or fall in relation to each other.
The high-pressure die-casting process entailed a decrease of carbonyl group peaks in relation to the ether and phenyl groups peak maxima. This shift of absorption intensities indicates a decrease in carbonyl groups, which could have been caused by decomposition or by a possible reaction with the aluminum. Basically, a reduction of carbonyl groups in neat PEEK polymer could result in an ordered polymer structure and by this a higher degree of crystallization. However, the clear change in the symmetry of the signals between the aromatic C-H vibration, i.e. 769 cm$^{-1}$ and 928 cm$^{-1}$, in the fingerprint area indicate the opposite [22]. In particular, the decrease of the peak at 769 cm$^{-1}$ proves a reduced crystallinity of PEEK in the interface.

Based on the results, the structural change of the PEEK in the interface region can be attributed to process-related thermal degradation processes. It is assumed that this, in the form of a thermally induced modification of the PEEK, enables the connection between PEEK and aluminum.

4. Conclusions
This work has shown that it is possible to produce a hybrid composite of CFRP, PEEK and the AlSi10MnMg aluminum alloy in an innovative way using the high-pressure die-casting process. Results prove that maximum tensile shear strengths of around 22 MPa can be achieved.

It has been showed by means of TEM and EDX analyses that the PEEK and the aluminum alloy form a gap-free bond in the direct contact areas where no outgassing is present. Microscopic investigations show no significant undercuts at micro- and nanometer level. In the contact area of both materials, a clear presence of the elements magnesium and oxygen could be detected at the nanometer level. These findings strengthen the suggestion that a potential connection of PEEK and AlSi10MnMg is made via MgO.

With regard to the thermal influence under process temperatures up to 700 °C, an XPS analysis showed that the PEEK is present in a structurally modified form in the contact area with aluminum. Even after treatment with solvent, more strongly adsorbed polymer layers could still be analytically detected for PEEK.

Analyses of the IR spectrum of PEEK in the contact area of both materials showed that changes in the polymer structure had occurred, which can be associated with initial degradation processes. There is a likelihood that initial degradation of the PEEK results further bonding possibilities of the PEEK to aluminum.

The results of this work allow a first description of the bond between PEEK and aluminum and the bond strengths obtained. Based on the investigations the form fit and the interdiffusion can be excluded. Especially the EDX and XPS analysis provide the first evidence that the bonding could be mainly based on interactions at a nanoscale level. Further investigations are required in future work. The interface between Al and PEEK should be investigated in more detail, e.g. using XRD analysis to characterize the MgO lattice structures described.

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