Influence of surface treatment on the bond strength of plastics/metal hybrids

The newly developed “integrated metal/plastic injection moulding” allows the manufacturing of plastics/metal-hybrids combining the injection moulding of plastics with the pressure die casting of metals on one machine. The materials plastic and metal are combined in a specially designed multi-component injection mould. In a first step the plastics preform is moulded. In the second step, the injection of the liquid low melting tin-zinc metal alloy enables the integration of full metal areas, preferably working as electrically conductive tracks. For applications in electric devices a certain bond strength between plastics carrier and metal conductor is demanded. This article is focused on different surface treatment techniques to improve the achievable bond strength between the thermoplastic and the metal component.

Einfluss der Oberflächen-Vorbehandlungs-methode auf die Verbundfestigkeit bei Kunststoff/Metallhybriden

Influence of surface treatment on the bond strength of plastics/metal hybrids

Ch. Hopmann, K. Bobzin, J. Wunderle, A. Neuß, P. Ochotta, Ch. Schulz, X. Liao

1 INTRODUCTION

State of the art in the injection moulding of plastics/metal-products are two major hybrid processing techniques: Post-mould-assembly and in-mould-assembly. Post-mould-assembly processes are commonly separated in two steps [1]. In the first step, the metal and plastics parts are produced separately, to be assembled in a following procedure. To create a solid and mechanically resistant connection between metal and plastic, the parts are for example welded, glued or screwed to each other in the second step. The in-mould-assembly process comprises a preceded production of the metal parts. The prefabricated metal parts are subsequently placed in the injection mould to be overmoulded with the plastic component. In each case especially the production of the metal component is characterised by additional expensive and complex procedures like bending, stamping, drilling etc.

The growing demand on highly integrated products manufactured in a short and efficient process led to the development of a new hybrid processing technique, called the "integrated metal/plastic injection moulding" (IMKS). The new technology is based on a standard injection moulding machine that is equipped with an additional, newly developed metal injection unit which allows the pressure die casting of low melting metal alloys (figure 1). Thereby the metal alloy is moulded and hence gets a primary forming character. In a first step the plastics preform is moulded. In the second step, the liquid low melting tin-zinc metal alloy is overmoulded. Due to the fine and complex conductive tracks that are to be moulded and the low mechanical properties of the metal alloy, the order of processing the plastic before the metal alloy is given. Changing the order would lead to deformation and destruction of the conductive tracks. Therefore the changed order is investigated in a partner research project that applies high-strength die-casting alloys [2].

By the use of the metal pressure die casting additional metal processing steps are eliminated and complex three-dimensional geometries of the metal parts are enabled. The integrated production of multifunctional parts, featuring additional freedom of forming the metal component, for electric and electronic applications in high volumes becomes possible without any preceding or following process steps.
In the electronic industry there is an enormous economic interest using a short process chain to produce plastics/metal parts [3]. The capability to substitute conventional manufacturing processes with the integrated metal/plastic injection moulding amplifies the importance of this new hybrid process. Variable classes of functional parts with circuit board similarity for automotive, health care or the telecommunications industries are producible. Furthermore, the new process enables the simple integration and contacting of electrical connectors such as plugs or electrical functional elements e.g. batteries, ICs and LEDs into the part. The applied tin-zinc is particularly suitable, because of its relatively high specific electrical conductivity of $8.9 \times 10^6$ S/m (copper: $5.8 \times 10^7$ S/m). Another possible field of application is based on the heat transfer coefficient of $61$ W/(m*K) (copper: $400$ W/(m*K)). For example heat sinks like cooling fins for the efficient transportation of heat energy can be integrated. Hence, in each of the considered fields of application, a solid connection between plastic and metal is needed to guarantee a reliable function of the plastics/metal hybrids.

One major research question is the resulting bond strength between the thermoplastic and the low melting metal alloy. Basically there is no direct adhesion between the materials to be suspected, so it becomes necessary to provide a surface modification on the plastic preform where the metal conductive track adheres to, the heat can be transported or the elastic plastics is connected to metal alloy [4]. For this purpose a range of different surface treatment methods were examined to find an adequate way of production to create a reproducible and mechanically loadable connection between plastics and metal for further applications.
2 MODELS FOR ADHESION BETWEEN PLASTIC AND METAL

There are various models and theories on adhesion. To understand the mechanisms of joining plastics and metal, the following six prominent adhesion theories are discussed of which five can be applied [5].

- Mechanical interlocking
- Thermodynamic (or adsorption) theory
- Chemical bonding theory
- Electrostatic theory
- Theory of weak boundary layers
- Diffusion theory

The basic principles of adhesion cannot be explained using just one single theory. Adhesive bonds are influenced by mechanical, physical, and chemical forces that influence each other. The mechanical theory of adhesion is based on an interlock between the components e.g. created by the filling of voids or pores on the surfaces. The thermodynamic (or adsorption) theory of adhesion, the most important mechanism of adhesion, attributes attractive forces between two materials to intermolecular interactions between molecules of each material [6]. The adhesive forces result from weak interactions that occur between molecules close together [7]. These physical interactions are called secondary force interactions. An example is the hydrogen bond which is an interaction between a hydrogen atom and an electronegative atom, such as nitrogen, oxygen or fluorine that is provided by another molecule. Chemical bonding theory describes adhesion of two materials that are held together by an ionic or a covalent bonding between molecules of each material which are called primary bonds. Chemical bonds formed across the adhesive-substrate interface can greatly participate to the level of adhesion between both materials [5]. According to the electrostatic theory, the adhesion forces are applied by contact or transfer potentials. These transfer potentials cause the build-up of an electric double layer at the interface and corresponding Coulomb attraction forces between the two components. The theory of weak boundary layers describes failures of bonds which are caused by an interfacial layer that is weakened by contaminations and not by failure of the bulk materials. Contaminations are for example air voids, reaction products like oxide layers or low molecular substances. Lastly the diffusion theory of adhesion is based on the assumption that the adhesion strength of polymers to themselves (autohesion) or to each other is due to mutual diffusion (interdiffusion) of macromolecules across the interface, thus creating an interphase [18]. As there is hardly any diffusion between metal and plastic expected, the diffusion theory of adhesion is not applicable for this specific kind of bonds. The other five theories of adhesion are applicable and in the following provide valuable approaches for the explanation of observed effects.
3 EXPERIMENTAL

3.1 Materials

Thermoplastic grades applied in electrical devices like Polyamide (PA 6.6, uncoloured) and Polybutylene terephthalate (PBT), table 1, are chosen for the experiments [19,10]. In addition to their different chemical composition these thermoplastics provide a range of different mechanical properties. Additionally glass fibre reinforced grades of these polymers with fibre content of 30 % are investigated.

The interaction between the injected metal alloy and the thermoplastic defines the selection of the overmoulded metal alloy. In order to protect the temperature-sensitive thermoplastic, a metal alloy with a melting point in the range of thermoplastics is necessary. The chosen metal alloy is composed of tin and zinc and made by MCP HEK Tooling GmbH, Lübeck, Germany. These alloys are used for lost core technology and rapid prototyping [11,12]. Through the eutectic composition of the alloy, a melting point about 200 °C is realized.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Plastics</th>
</tr>
</thead>
<tbody>
<tr>
<td>tin-zinc-alloy</td>
<td>Polyamide 6.6 (PA 6.6)</td>
</tr>
<tr>
<td>(MCP 200)</td>
<td>Polyamide 6.6 with 30% glass fibre (PA 6.6 GF30)</td>
</tr>
<tr>
<td></td>
<td>Polybutylene terephthalate (PBT)</td>
</tr>
<tr>
<td></td>
<td>Polybutylene terephthalate with 30% glass fibre (PBT GF 30)</td>
</tr>
</tbody>
</table>

*Table 1: Overview of the investigated materials*

3.2 Surface Treatment Methods

In order to be able to evaluate the bond strength, plastics/metal tensile bars, as shown in figure 2, are produced in a hybrid injection mould using the integrated metal/plastic injection moulding”. Therefore the plastic part of the specimen is moulded in a first step. In the second step this plastics preform is transferred to another cavity of the mould where the part is overmoulded with the low melting metal alloy. Figure 3 shows the injection mould used for this process. The chosen sequence accommodates the fact that the metal alloy has to be the second component when moulding sophisticated metal structures such as electrically conductive tracks. In a reversed sequence (metal alloy first, overmoulded with plastics) these delicate structures would not be strong enough to withstand the pressure load during the plastics injection. In a first test series the plastics specimen remains untreated. In further experiments plastics preforms are taken out of the mould to be surface-treated prior to the
overmoulding step. Surface treatments are done using three different techniques: The atmospheric pressure plasma treatment, the laser treatment and the metal spraying.

Figure 2: Specimen consisting of thermoplastic and low melting metal alloy

Figure 3: Injection mould used for the production of hybrid tensile bars
3.2.1 Atmospheric Pressure Plasma

The first method is the inline treatment with atmospheric pressure plasma. Figure 4 shows a schematic of the plasma head.

In this method compressed air is blown through a single electrode which discharges inside the head of the device. The air is ionised by the electric arc created in the head and transported to the specimen [13,14]. Through the bombardment of the specimens surface with ions and electrons the surface is activated and possible contaminations are removed mechanically and chemically [15,16,17]. The plasma device moves over the specimen at a velocity of 180 mm/s (feed rate). The distances between plasma nozzle and specimen are adjusted empirically with the objective that the plasma treatment has no visual effect on the surface. Typical distances range between 8 mm to 12 mm. The surface temperature of the specimen during the procedure is below 80 °C so that the plastics surface is not weakened by degradation.

3.2.2 Compressed air assisted laser treatment

For the laser treatment a CO₂ laser is used with an emission wavelength of 10.6 microns as plastics surfaces generally have a low optical depth (~ 10 microns). In order to create an undercut without burning the plastic the laser beam heats up and reduces the viscosity of the plastic, so it can be blown out by compressed air to create a fine groove.
Using this method geometrically similar structures are created which work as micro undercuts in the plastics surface. Undercuts are subsequently filled by the metal alloy during overmoulding and create a form closure between the two components. As presented in figure 6, the pictures of scanning electron microscope show the surface of a laser treated polymer specimen. Between the gaps the later injected metal alloy can creep in. The undercuts are perpendicular to the direction of force during the tensile test.

**Figure 5: Schematic of the laser treatment**

**Figure 6: Surface of the plastic specimen after laser treatment. Left: PA 6.6; Right: PA 6.6 GF 30, bottom: PA 6.6 (macroscopic view)**
The parameters for the laser treatment are listed in table 3. The diameter of the air jet nozzle, the distance between laser and plastic surface, the wattage of the laser and the distance between the gaps created are constant. The feed rate describing the speed the laser is moving over the surface is varied.

<table>
<thead>
<tr>
<th>Material</th>
<th>Air jet diameter [mm]</th>
<th>Distance to surface [mm]</th>
<th>Wattage [W]</th>
<th>Gap distance [mm]</th>
<th>Feed rate [mm/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBT</td>
<td>1.5</td>
<td>3</td>
<td>20</td>
<td>0.5</td>
<td>100</td>
</tr>
<tr>
<td>PBT GF30</td>
<td>1.5</td>
<td>3</td>
<td>20</td>
<td>0.5</td>
<td>40</td>
</tr>
<tr>
<td>PA 6.6</td>
<td>1.5</td>
<td>3</td>
<td>20</td>
<td>0.5</td>
<td>100</td>
</tr>
<tr>
<td>PA 6.6 GF30</td>
<td>1.5</td>
<td>3</td>
<td>20</td>
<td>0.5</td>
<td>60</td>
</tr>
</tbody>
</table>

Table 2: Parameters of laser treatment

3.2.3 Arc spraying

The third method is the coating of the thermoplastic surface with a thin layer of zinc before the injection of the metal alloy. This rough layer offers micro undercuts where the later overmoulded low melting metal alloy can creep in. An additional benefit is that the low melting metal alloy also contains zinc, so a better compatibility is expected. Figure 7 shows the schematic of the metal spraying process. The zinc coat is brought in by a metal spraying process (wire arc spraying) and represents an intermediate layer between the metal alloy and the thermoplastic specimen. In the arc spraying process, a spray of molten metallic particles is created using compressed air in combination with continuously melting zinc wires. The zinc wires are fed into an electrical arc formed between the wires. Due to the high velocity and temperature of the zinc particles generated by the arc spraying process, some of these particles have sufficient energy to hit and deform on the surface of the plastic specimen. By this impact, an interlock between the plastic specimen and zinc layer is generated. Due to its melting temperature of 420 °C the zinc layer does not remelt during the overmoulding process. In the experiments two different zinc coat thicknesses (100 µm, 200 µm) and the following spraying parameters are used: Voltage 21 V, current 150 – 180 A, pressure of compressed air 3.5 bar, distance between specimen and nozzle 150 mm, traversing speed 800 mm/s.
4 EXPERIMENTAL CHARACTERISATION

In the following sections the tensile strength of single material specimens and the bond strength of the composite specimens, the plastics/metal tensile bars, is tested. Both values are measured by a tensile testing machine Zwick BZ010/TN2A of the Zwick GmbH & Co. KG, Ulm, Germany, using a tensile speed of 50 mm/min. The test of the composite specimens is done similar to the DIN 53 283 that is used to verify adhesive bonds. As adhesive bonds are generally more resistant against pressure and tensile loads, the chosen test specimen applies a tensile shear load to the interface. While the test of the single material specimens is based on a pure tensile load, a comparison within the single materials is gained.

Regarding the bond strength of the composite specimens, firstly, the different surface treatment methods are applied to the plastics, injection moulded part. After the surface modification, the metal alloy is overmoulded and the parts are tested. The die casting parameters are shown in table 3.

<table>
<thead>
<tr>
<th>Mould Temperature</th>
<th>100 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydraulics pressure</td>
<td>55 bar</td>
</tr>
<tr>
<td>Specific die-casting pressure</td>
<td>280 bar</td>
</tr>
<tr>
<td>Crucible temperature</td>
<td>290 °C</td>
</tr>
</tbody>
</table>

Table 3: Die casting parameters of the metal overmoulding.
To avoid after shrinkage effects the injection moulded parts are stored for 24 hours before the surface modification and the subsequent metal overmoulding. The finally produced parts are stored again for 24 hours before the destructive testing.

4.1 Tensile properties of the single material

To create a reference, in a first test series the maximum force before breaking of the single material specimens is measured (figure 8). Single material halves of the hybrid tensile bars, figure 2, are used for these tests.

As expected, the fibre reinforced plastics show a higher maximum force than the unreinforced. The MCP 200 is on a similar level as the PBT without glass fibres and below the maximum force of the pure PA 6.6.

In the second test series, untreated plastic specimens are overmoulded with the low melting metal alloy for each polymer. A solid bond between metal and PBT is not observed or, in case of the PA 6.6 and PA 6.6 GF30, the bond strength is on such a low level that the bars already break during demoulding. The stickiness may result from a reduction of the polymer chain length in the interface due to induced temperature of the overmoulded metal alloy. The effect of high temperature (250-300°C) leading to a lower molecular weight and a better bond strength between metal and PA 6.6 was observed by Flock [18] using the gel permeation chromatography. In the experiments the “heat conduction bonding” was developed, using the same polymers as shown in table 2. The effect was not observed when using the same temperatures for the
PBT. Using the “heat conduction bonding” a heated metal part is pressed onto the polymer part to create directly bond strength without bonding agent.

4.2 Influence of the Plasma Treatment

In figure 9 the maximum force of the plasma treated composite specimens is shown. After the surface treatment the bond strength is significantly higher.

![Comparison of the maximum force of plasma pre-treated composite specimens](image)

However, the bond between PBT (without glass fibre) and MCP 200 is just temporary. In a time of 12 hours after demoulding the tensile bares break without any external mechanical influence. This phenomenon can be explained with the post shrinkage of the PBT or probably because of missing nitrogen. In contrast the glass fibre reinforced PBT with lower shrinkage shows permanent bond strength. Figure 10 shows the comparison of the expected volumetric shrinkage of unreinforced and glass fibre reinforced PBT while production. This is generated by the mould filling simulation tool Cadmould 3D-F of the simcon kunststofftechnische Software GmbH, Würselen, Germany.

Figure 10 shows two plastic parts of the specimen (PBT GF30 top, PBT bottom). In the right area of both the injection gate is visible. The metal alloy is later overmoulded over the left area of the parts. In this area shrinkage of about 0.5 % is expected for reinforced PBT GF30. The shrinkage for the unreinforced PBT is significantly higher with an expected shrinkage value of about 2.2 %. Although the main shrinking process is finished after moulding the plastic parts, still post shrinkage can be expected which is naturally higher in unreinforced specimens.
Figure 10: Comparison of the expected shrinkage of reinforced PBT GF30 (top) and unreinforced PBT (bottom).

Figure 11: Temperature dependent specific volumes of PA 6.6 and PBT.

It is noticeable that PA 6.6 does not show the same behaviour although its overall shrinkage is comparable to that of PBT, figure 11. In order to investigate this disparity and to further analyse the effect of the plasma treatment the surface energies are measured. The surface energies of the untreated composite specimens and plasma treated specimens (PL) are shown in figure 12 separated in a polar (dipole force) and a dispersive (van der Waals forces) fraction.
All untreated specimens show that the disperse fraction of the surface energy is dominating which is typical for polymers. This reduces the wettability of the plastics surfaces by the MCP 200. PBT and PBT GF30 in this case show the highest disperse fraction and the lowest total surface energies. The high values of the disperse fraction are one reason that none of the untreated specimens show a measurable adhesion.

In comparison to PA 6.6 the polar fraction of PBT is considerably smaller. This disparity results from the difference in the chemical properties of these materials. The proportion of polar surface energy is due to permanent dipole-dipole reciprocities, which are able to form greater adhesive forces than temporarily fluctuating dipole-dipole reciprocities based on the disperse distribution of the electrons within a molecule. The cause of this is found within the molecular structure of the polyamide. The nitrogen atom in the molecular structure has a very high electro-negativity. This means that the electron in a covalent bond with the hydrogen atom is attracted stronger by the nitrogen atom. The atomic core of the hydrogen atom is thereby highly insulated and forms a strong positive permanent dipole. Approaching an oxidised metal element can cause strong hydrogen bridge bonds between the metal element and the polymer. PBT has no nitrogen atom in its molecular structure so that the majority of the adhesion forces between PBT and the metal element consist of the relatively weaker dispersion forces. The strong hydrogen bridge connections in the case of polyamide can better compensate for the ensuing shrinkage forces.
It is hard to isolate the different values to quantify their influence on the adhesion. Until now there is no suitable test method or innovative analysis for the quantification and separation of physical and chemical interactions in the boundary layer [19].

Plastics specimens pre-treated with atmospheric pressure plasma show an increased surface energy in the polar fraction. The growth of energy is based on additional polar functional groups on the surface. Regarding the tests of PA 6.6 and PA 6.6 GF30 a higher maximum force of the unreinforced specimens is observed. In this case the measured surface energy can give an answer. After a theory developed by Zisman, Fowkes and Good [19,20,21] the wetting process founds the basis for the thermodynamic theory of the adhesion. For the unreinforced PA 6.6 the polar fraction increases at the expense of the disperse fraction stronger than for the PA 6.6 GF30. In general, this could improve the wettability. However, the small difference of the polar fraction is in the range of the measurement inaccuracy.

To investigate the influence of the plasma, untreated and plasma treated preforms are surface analysed with X-ray Photoelectron Spectroscopy (XPS) to verify a change in the chemical composition of the surface, figure 13.

As expected, XPS analyses of the surface of plastic substrates which have been previously treated with atmospheric-pressure plasma particularly show an increase of the oxygen portion and a reduction in the carbon portion. This results in a greater reactivity of the surface for example for the formation of hydrogen bonds. Like in the surface energy analyses, the XPS analyses (figure 13) show the unreinforced PA 6.6 is more receptive to the plasma treatment than the PA 6.6 GF30. Correspondingly higher adhesion forces can be reached with the unreinforced PA 6.6. The oxygen concentration of the PA 6.6 surface could be increased from 10.8 % to 27.9 %, while PA 6.6 GF30 increases from 12.2 % to 24 %.
To be sure the plasma treatment has no additional roughening effect on the surface and provides no undercuts for the overmoulded metal, different methods to measure the roughness are applied. Therefore plasma treated and untreated specimens are examined regarding their surface topography using a MicroGlider from FRT GmbH, Bergisch-Gladbach, Germany. The MicroGlider is equipped with a chromatic sensor which illuminates the specimen using a white-light source and measures the wavelength-dependent (chromatic) distribution of the reflected light. By this distribution the integrated software determines the absolute height information. In table 4 the roughness of the PA 6.6 specimen before and after the plasma treatment is shown. As described before the

Figure 13: XPS investigations for the influence of a surface treatment with atmospheric pressure plasma
specimens are treated at different distances between plasma nozzle and specimen in order to avoid visible surface markings.

<table>
<thead>
<tr>
<th>Surface roughness</th>
<th>untreated</th>
<th>Plasma treated: s = 10 mm; v = 180 mm/s</th>
<th>Plasma treated: s = 8 mm; v = 100 mm/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ra1 [µm]</td>
<td>1.235</td>
<td>0.639</td>
<td>0.749</td>
</tr>
<tr>
<td>Ra2 [µm]</td>
<td>1.431</td>
<td>0.832</td>
<td>0.861</td>
</tr>
<tr>
<td>Ra [µm]</td>
<td>1.333</td>
<td>0.736</td>
<td>0.805</td>
</tr>
</tbody>
</table>

Table 4: Comparison of the roughness of a PA 6.6 specimen surface before and after plasma treatment

The surface roughness is averaged along the two crossing diagonals over the plasma-treated area of the specimen. From the measured values of the two diagonals the mean roughness values Ra1 and Ra2 are calculated as the value of surface roughness for the entire sample. Since the values in table 4 are average of thin lines, only a qualitative statement about the influence of plasma on the surface roughness is possible. The decrease in surface roughness as a result of plasma treatment can be considered as significant. The change in plasma intensity does not significantly affect the surface roughness. The surface smoothening influence is corresponding with investigations of Greenwood et. al. [12]. Other investigations show that rough surfaces are smoothened but already smooth surfaces show no change in the surface roughness. These phenomena are explained with the temperature of the plasma. Though the overall surface temperature is comparatively low (ca. 80 °C) the thermal energy transferred by the plasma suffices to melt possible roughness peaks in the micro range due to the very small heat capacity of such small structures. Also the temperature provides enough energy to enable near-surface recrystallization which again leads to a smoothing effect [13,14]. Hence, a roughening effect and possible micro gaps are not detected.

While there is no explanation possible for the increased bond strength by the surface roughness, the changed chemical composition and the modified surface conditions can give an answer. Regarding the results of the surface energy analysis and the XPS analyses the effect of the plasma treatment can be mainly explained based on the thermodynamic theory (better wetting) and the better conditions for secondary force interactions like hydrogen bonds because of the higher reactivity of the surface.
4.3 Influence of the compressed air assisted laser treatment

The laser micro-structuring is applied using varying process parameters adapted to the treated material. Hence, there is no uniform laser structure for all four polymers expected. In figure 14 the cross-section of the specimen show laser structures with varying structural depth depending on the polymer applied. Due to the lower varying feed rate during the laser treatment the glass fibre reinforced polymers show the deepest structures.

![Figure 14: Cross-sections of specimens with laser structures of varying structural depth](image)

An influence of the structural depth has to be taken into account if the specimens break in the intermediate layer (adhesive fracture). An adhesive fracture is observed for the material combination MCP 200 and PA 6.6 where the structural depth was obviously too low. Even though the PBT sample had the same structural depth, it and the remaining two material combinations break in the plastic part or in the metal part of the specimen (cohesive fracture). This means that the intermediate layer is not the weakest part of these specimens. Figure 15 shows the average maximum forces of laser structured composite specimens.
Figure 15: Comparison of the maximum force of laser pre-treated composite specimens

Generally the breaking forces are significantly lower than breaking forces of the single materials, figure 7. The reason is most likely the weakening through the laser formed gaps that create a notch effect. The notch effect can influence the mechanical strength of the plastic part negatively and also the metal part can be weakened.

The two glass fibre reinforced plastics reach similar maximum forces at an average of 2300 N. However the two results cannot be compared, because the test series with PA 6.6 GF30 shows cohesive fracture within the MCP200 part while the PBT GF30 shows cohesive fracture in the plastic part. Also the clamping situation seems to influence the reachable maximum forces of the specimens. The single material specimen which are fixed through the clamping on both ends show higher average values than the composite specimens where just one end of the MCP 200 is fixed through the clamping and the other end is bound to plastic. So obviously the application of force and the additional torque brought into the specimen differ from the tensile test done with the single material specimens and have a weakening effect on all composite specimens. Therefore a quantitative comparison between composite and single material specimens is not allowed.

Furthermore the composite specimens made of PBT GF30 and MCP 200 show a cohesive fracture within the plastic part beneath the maximum force of single MCP 200, despite the single material plastic specimens showing a significantly higher maximum force than single material MCP 200 specimens. An explanation for this result can be the brittle behaviour of the PBT which in combination with the notch effect of the gaps and additional torque leads to a
faster failure of these specimens. Corresponding failure mechanisms occur in the composite specimens made of PBT and MCP 200.

### 4.4 Influence of the metal spraying treatment

In this test series the plastics surfaces are coated with zinc by an arc spraying process before overmoulding with MCP 200. The tensile tests, just like the laser-structured samples, show adhesive and cohesive fractures. As the sprayed zinc coat provides an intermediate layer between the plastics and MCP 200 working as a kind of bonding agent, the place where the adhesive fracture takes place has to be analysed. While the adhesive fracture of the laser structured specimens is located directly in the intermediate layer, the adhesive fracture of the zinc coated specimens can be found between zinc and MCP 200 and also between zinc and plastic. If the layer between plastic and zinc coating fails, subsequently just the bond strength between plastics and zinc can be evaluated. Also a failure at the interface zinc and MCP200 makes the bond strength of zinc/MCP evaluable. A mixture of failure in the interfaces of zinc/MCP and zinc/Polymer occurred in the specimens PA 6.6, PA 6.6 GF30 and PBT GF30 that indicates a good adhesion to both materials. The brittle PBT specimens failed cohesive in the plastics part. Regarding the specimens with the mixed fracture the plastics surface always shows small zinc particles left on the surface, figure 16.

![Figure 16: Adhesive fracture of metal sprayed composite specimen (PA 6.6) at different interfaces](image)

Also different zinc coat thicknesses are applied to create gaps of different depth in which the MPC 200 can crawl in. As shown in figure 17 in three of four cases the thicker zinc coat leads to specimens with lower mechanical properties. This can be explained by the porous structure of the zinc layer that weakens its basic strength, figure 18.
Just for the PBT GF30 a thicker zinc layer offers a better bond, marking the best bond strength of the metal spraying test series. Again the fibre reinforced grades show higher values in the tensile tests. However, reliable information about the influence of the zinc layer thickness cannot be gained due to broad distribution of the results. The only material where the bond strength leads to relative constant but low values is the unreinforced PA 6.6.
5 DISCUSSION

The comparison of the different surface treatment methods under variation of the two polymers with and without fibre reinforcement is shown in figure 19. The wide spreading results state a strong dependence of the reachable bonding strength on the plastics and the applied surface treatment.

Starting with the unreinforced PBT the best method is the zinc coating with a layer thickness of 100 µm, however, with unstable results. Thicker zinc coats lead to lower values. The laser treated specimens achieve lower maximum forces than the metal sprayed. This is the lowest maximum force of all measured specimens. As mentioned the notch effect in combination with the brittle behaviour of the PBT are most likely the reasons for the low maximum forces. The plasma treated specimens cannot compete as no lasting bond occurs due to the high shrinkage potential. For the PBT GF30 the highest value is reached with a composite specimen that is equipped with the 200 µm zinc coat, however, the laser treated samples are on a higher average level. The PA 6.6 shows the highest maximum force before breaking with the plasma pre-treated specimens. The laser structured specimens are on the same level as the zinc coated. The PA 6.6 GF30 shows the highest overall result with the laser structured specimens. The zinc coated specimens with the 100 µm layer have also high maximum forces, however the results are unstable.

Comparing the fibre reinforced polymers, the most reliable and comparatively highest maximum forces are achieved using the laser treatment generating gaps on the plastics surface. The higher strength of the reinforced polymers allows to create a strong basis of gaps that work as anchorage points for the metal. In case of the unreinforced polymers the created gaps have a weakening effect. The overall results also underline the potential of the plasma treatment (except for the unreinforced PBT). As shown the plasma treatment generates better conditions for adhesion. The improved surface energy composition with a lower disperse fraction and a higher polar fraction and also the higher concentration of oxygen on the surface are possible reasons for the increased bonding strength.
6 CONCLUSION AND OUTLOOK

The new developed integrated metal/plastic injection moulding offers the possibility to create plastics/metal parts using one modified injection moulding machine with a dedicated mould technology. In comparison to existing process chains, the number of process steps is reduced to one single injection moulding cycle with two consecutive injection phases. This enables to manufacture plastics/metal parts especially with electronic functionality in extraordinary short cycle times. Different methods of surface treatment were tested to improve the bond strength between the, in general, non-adhesive mould materials.

The methods for producing a strong bond are compared below with respect to their industrial relevance. The investigations stated that with all pre-treatment methods the bond strength can be increased. Since the values of the tensile test are unstable in some cases, just qualitative statements about the influence of pre-treatment methods on the bond strength are possible. Another challenge for the evaluation of the real bond strength is the cohesive failure. In the cases of cohesive failure, the identified bond strength is a product of failure in an area not allocated at the interface metal/plastics which leads to an additional variation regarding the results. This problem could be addressed by utilizing different specimen geometries with a smaller contact area between the plastics and metal parts thus ensuring that the weakest part of the specimen is in fact the intermediate layer. With the compressed air assisted laser treatment two parameters showed a significant influence to the reachable bond strength: The feed rate of the laser having a decisive influence on the depth of the groove and the fibre content of the polymer which reinforces the created anchorage point.

The laser treatment marks the only method of the investigated pre-treatment that relies on a real interlock between metal and plastic. This micro creeping basis guarantees maximum forces on high levels for all plastics. Only for the unreinforced PBT it is not the appropriate method. However, the surface changing property of the laser treatment can be restrictive if the surface must stay in its original shape. The plasma treatment in this case has the benefit that the surface shape is not being modified in a visible way. The change happens on molecular level which leads to higher surface energies and a better wetting behaviour. The plasma leads to a good bond strength which for unreinforced PA 6.6 even beats the laser treatment method. Additionally it can be assumed that the integration of the plasma treatment method into the production is comparably simple. The plasma treatment does not work for unreinforced PBT. The weaker bond can be explained by the missing nitrogen atom, hence a majority of the adhesion forces between PBT and the metal element consist of the relatively weaker dispersion forces. Also in comparison to the PA 6.6 the molecular weight of PBT is not reduced significantly through the short temperature load, which could lead to a stickiness of the surface, as seen in experiments using the same materials to the heat conduction bonding.

The wire arc spraying method needs an additional process step for the surface treatment. The zinc layer as bond agent works especially for the PBT GF30.
However, the results are unstable so that some optimization is necessary to gain reproducible results. Reliable results occur just for PA 6.6.

Further investigations regarding the mechanical properties will be focused on long-term properties, chemical resistance and resistance to temperature changes.
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Bond strength of plastics/metal hybrids

**Stichworte:**
hybride Mehrkomponenten-Spritzgießverfahren, Oberflächenbehandlung, Adhäsion, niedrig schmelzende Metalllegierung, Atmosphärendruckplasma, Lichtbogen Spritzen, Pressluftlaserbehandlung

**Keywords:**
hybrid multi-component injection moulding, surface treatment, adhesion, low melting metal alloy, Atmospheric Pressure Plasma, Arc spraying, Compressed air assisted Laser treatment