Influence of Plasma Coating Pretreatment on the Adhesion of Thermoplastics to Metals

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Abstract. Combining metal sheets and thermoplastics into hybrid structures is a promising approach to design geometrically complex and highly durable lightweight parts. To ensure an economical production of these hybrid structures, the metal component can be overmoulded with a thermoplastic compound in an injection moulding process. Due to the dissimilarity of the materials, a suitable pretreatment of the metal sheet is required to ensure proper adhesion of the components. Plasma technology can be used to apply an adhesion promoter based on a precursor onto the metal surface. Furthermore, plasma pretreating can be integrated into the automated process chain. Additionally the metal sheet has to be preheated to activate the adhesion promoter. Besides the preheating temperature of the metal insert, the process parameters of the precursor application and the injection moulding process influence the adhesion strength of the joint between the metal and the thermoplastic. To identify the process window for sufficient adhesion, parameter studies based on a design of experiments are carried out. The manufactured hybrid test specimens are tested according to DIN EN 1465 for mode 1 shear strength. Additionally, the failure mode is evaluated by optical analysis. As a result, a correlation between the process parameters of plasma pretreatment and the structural property shear strength is derived.

Keywords: Hybrid composite structures · Adhesion · Shear strength · Plasma pretreatment · Overmoulding

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1 Introduction

The EU confirms the zero CO_2 road mobility target by 2035, for which reason only zero-emission vehicles - preferably battery-electric or hydrogen-powered vehicles - will receive new registrations from 2035 [1, 2]. With this sign of transformation, the demands on the resource efficiency of individual mobility increase. Lightweight engineering, especially by innovative lightweight design, new types of materials and material combinations can make a significant contribution to achieving this aim [3, 4]. Here, multi-material components made of metal, endless fibre-reinforced plastics (FRP) and injection moulding compounds present a promising approach.

Metal substructures are predestined for areas subjected to multiaxial loads; the areas with directional load paths can be specifically reinforced with FRP [6]. The combination with the injection moulding process allows additional functionalisation, for example with screw domes, snap-in hooks or stiffening ribs combined with economic process times.

The combination of thermoplastic FRP and injection moulding compound into hybrid structures has been extensively researched in recent years [6–10]. As a result, customised, multifunctional and geometrically complex lightweight structures can be manufactured by the combination of FRP and injection moulding technology.

The main challenge in the development, production and use of hybrid structures is the design of the interface between the different materials. If a material bond is to be created between the FRP and the injection moulding compound, the FRP must always be pretreated, usually by heating it to above the melting temperature of the matrix [11]. The bonding strength between the thermoplastic components is achieved by the interdiffusion of the molecules and depends in particular on the type of matrix polymers, the temperatures of the FRP and the injection moulding compound as well as mould temperature [10, 12–16]. In addition to the process parameters, the geometry of the rib base also influences the load-bearing capacity. For instance, numerical and experimental studies have shown that for the same rib geometry, a wide rib base significantly increases the effective load-bearing capacity of the bonding zone compared to blunt rib base [14, 16, 17].

Previous research has demonstrated the lightweight potential of this hybrid design compared to classical metal structures, as well as the possibility of realising highly loadable structural components such as crash-relevant vehicle parts [5, 18, 19]. In contrast to FRP, injection moulding hybrids without metal inserts, the surface of the metal component needs to be modified to ensure a high bonding strength between metal and injection moulding compound or FRP [20]. In addition to macroscopic or microscopic interlockings [21, 22], adhesion promoters in the form of films or coatings are also used [22, 23], showing that these pretreatments can lead to highly loadable joints [24]. However, the pretreatment effort is often high, which means that these methods are not yet suitable for inline treatment of the metal surface within the cycle time of the injection moulding process. Plasma technology is an alternative to the methods mentioned. With this process, metal surfaces are cleaned and pretreated quickly and automatically. In addition, an adhesion promoter can be deposited by plasma polymerisation of precursors on the surfaces to improve the adhesion between metal and thermoplastic [25].

Thereafter, the coated metal inserts must be heated before overmoulding with injection moulding compound, pressed or printed with FRP in order to achieve high bonding strength [26].

The aim of this paper is to investigate the influence of the precursor application parameters and the metal preheating on the bonding strength between injection moulding compound and a plasma pretreated metal insert.

2 Materials and Methodology

2.1 Materials

The steel insert is made of a cold-rolled low alloyed steel (HC 420 LA). The used precursor (PT-Bond 1300.1, from Plasmatreat GmbH, Seinhagen, Germany) acts as a chemical adhesion promoter. In order to increase the bonding strength, a precursor adapted injection moulding compound based on modified polyamide 6 (AKROMID® B3 GF 30 1 PST black (6647), from AKRO-PLASTIC GmbH, Niederzissen, Germany) is used.

2.2 Manufacturing Process

The manufacturing of the test specimens comprises the following main steps: chemical cleaning, plasma cleaning and coating, preheating and injection moulding.

Chemical Cleaning. As the cold-rolled steel HC 420 LA is prone to oxidation, an oil film is applied after the manufacturing for delivery and storage. In order to achieve bonding between the precursor and the metal, a two steps chemical cleaning process is performed. First, the coarse contaminations are removed by isopropanol and wiping with paper cloth until no residues remain. Afterwards, the metal is flushed with isopropanol and left for drying, to avoid contamination by the paper cloth.

Plasma Cleaning and Coating. To achieve an ultra-fine cleaning of the metal surface, the specimens undergo a robot-guided (KR6, from KUKA Industries GmbH, Augsburg, Germany) plasma cleaning sand coating process (Fig. 1). The parameters of the plasma cleaning are shown in Table 1.

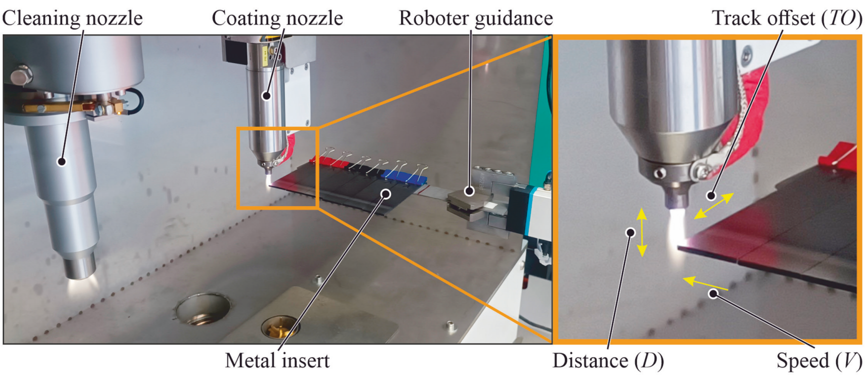

Fig. 1. Plasma cleaning and coating process.

Table 1. Parameter set for plasma cleaning and coating process.

Parameter	Cleaning		Coating
Voltage in V		290	
Frequency in kHz		21	
Plasma cycle time in %		60	
Ionization gas flow in l/min	60		33
Carrier gas flow in l/h	N/A		300
Precursor mass flow in g/h	N/A		6
T piece temperature in °C	N/A		175
Jet head temperature in °C	N/A		110
Vaporizer temperature in °C	N/A		340

Preheating. For the preheating of the metal insert (Fig. 2) an injection moulding tool equipped with two additional 450 W heating cartridges (MISF19002B, from Hotset GmbH, Lüdenscheid, Germany) was used. To achieve the minimum Temperature of 80 ℃, the metal insert was preheated for 30 s prior overmoulding by the tooling temperature. The temperatures of 160 ℃ and 240 ℃ were realized with 90 s and 240 s preheating time by the additional heating cartridges, which enable a local heating of the bonding area (Fig. 2 right).

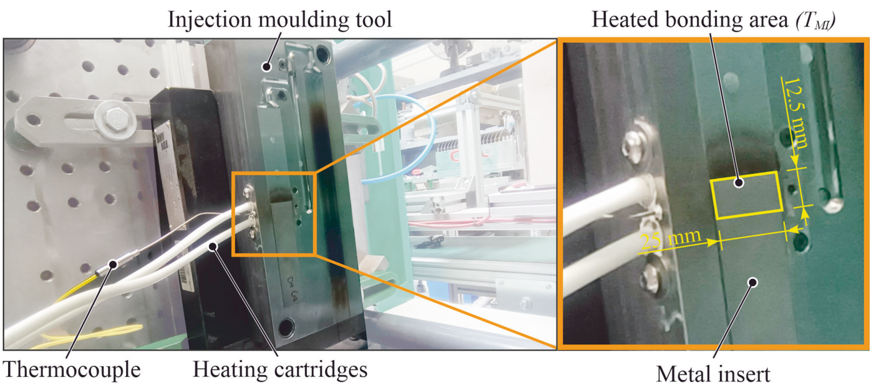

Fig. 2. Injection moulding tool with integrated heating cartridges.

Injection Moulding. For overmoulding an Arburg 370H (Allrounder 370H 600-290, from Arburg GmbH+Co KG, Lossburg, Germany) injection moulding machine was used. The process parameters are summarized in the Table 2. To prevent oxidation and moisture absorption by the polyamide 6 all hybrid test specimens were kept in dry bags until testing.

Table 2. Injection moulding process parameters.

Injection speed	Packing pressure	Holding pressure	Cooling time	Injection mass temperature
150 cm^3/s	1200 bar	550 bar	30 s	280 °C

2.3 Design of Experiments

To investigate the relationship between the process parameters and the structural properties, a two-level full factorial design (FFD) with a central point was chosen. After the analysis of the manufacturing process [27], 81 process parameters were identified that could have an impact on the bonding strength. For the experimental design (Table 3), these parameters were further reduced to four factors by taking the manufacturing and economical restrictions into account. The speed (*V*) and track offset (*TO*) of the plasma nozzle are selected (Fig. 1 right), as these factors are important to reduce the pretreatment time and therefore to increase the efficiency. The distance (*D*) of the plasma nozzle to the metal surface is relevant (Fig. 1 right), as highly complex metal parts restrict the required clearance of the plasma pretreatment process. To account for different preheating technologies and therefore the maximum achievable temperatures within reasonable time, the temperature of the metal insert (T_{MI}) was selected (Fig. 2 right).

Table 3. Variation of the factors for the 2^4 – FFD.

Factor	Level−	Level 0	Level+
Speed in m/min	4	12	20
Track offset in mm	1	5	9
Distance in mm	4	12	20
Metal insert temperature in °C	80	160	240

2.4 Mechanical Testing

To determine the shear properties with sufficient statistical certainty six test specimens of each configuration are tested under standard climate of 23 ℃ and 50% relative humidity. To prevent mix mode loads during the tensile testing [28], a specific compression shear testing device [28] is used. By redirecting the tension forces introduced by the testing machine (Zwick Z100, from ZwickRoell AG, Ulm, Germany), to the compression edge of the compression shear testing device, primarily shear stresses occurs within in interface of the joint.

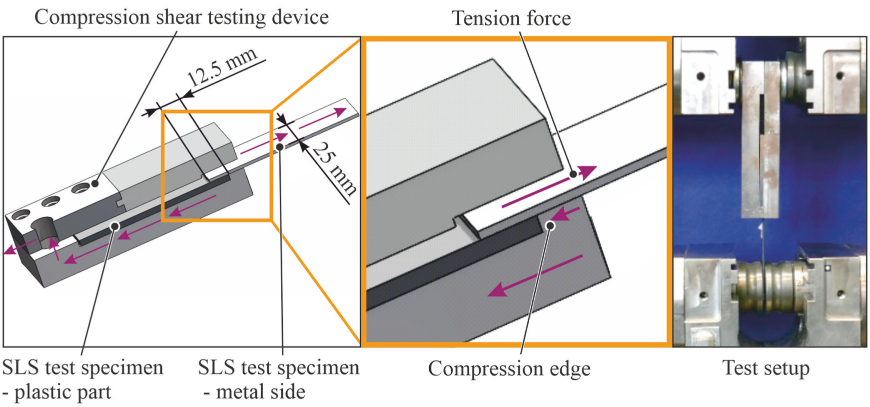

Fig. 3. Compression shear testing device (left and centre) [29] and test setup (right).

The force occurring during the test was recorded using a calibrated 10 kN load cell (Z12, from Hottinger Brüel & Kjaer GmbH, Darmstadt, Germany) and compared with the corrected crosshead travel measurement data. The measurements are recorded up to a force drop of 80% at a testing velocity of 2 mm/min in according to DIN EN 1465:2009.

3 Results and Discussion

3.1 Test Results

The results obtained can be divided into two categories: adhesive (left side) and cohesive (right side) failure, as shown in Fig. 4. No combination of the factors: distance, speed and track offset leads to adhesion at the preheating temperature of $T_{MI} = 80$ ℃ (test series 1 to 8) of the metal insert. At the centre-point, $T_{MI} = 160$ ℃ first bonding between the precursor and the injection moulding compound appears with a mean value of 6 MPa. For all factor combinations performed at $T_{MI} = 240$ ℃, adhesion with cohesive failure occurs. Both the mean values and the scattering depend on the combination of the values of *V*, *TO* and *D*. The lowest bonding strengths of 2.75 MPa mean value emerge at low *V* and *D* in combination with a narrow *TO*. The highest values between 30.3 MPa and 41.6 MPa bonding strength are achieved with the *V* of 4 m/min, *D* of 20 mm and *TO* settings of 1 mm.

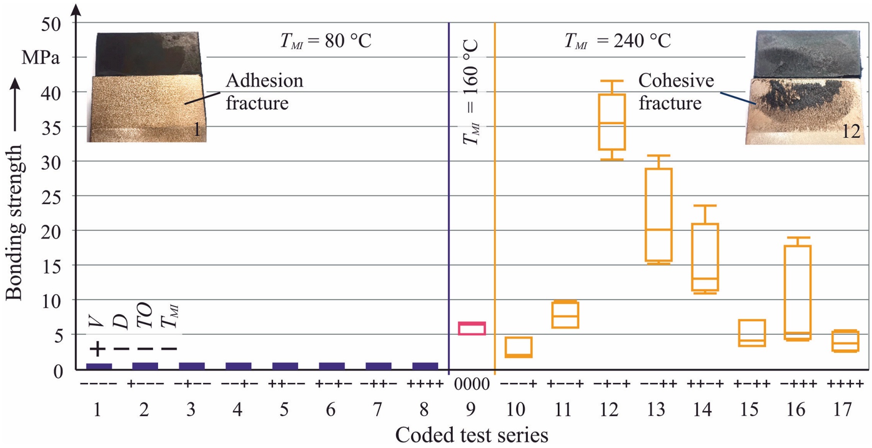

Fig. 4. Test results for the 2^4 – full factorial design.

For the test series 1 to 8 (Fig. 4), performed at low preheating temperature of the metal insert, only adhesion failure occurs (Fig. 4, top left corner). Small amounts of plastic residuals appeared on metal surface after testing for the series 9 to 11 as well as 15 and 17. The fracture surface of the test series 13, 14 and 16 indicates a mixture of adhesive failure between the metal and injection moulding compound as well as cohesive failure of the thermoplastic itself. A factor combination performed in the test series 12 causes fracture behaviour dominated by cohesive failure of the reinforced thermoplastic (Fig. 4, top right corner).

3.2 Statistical Modelling of Parameter Interactions

The first step to achieve a prediction model [30] of the bonding behaviour was to identify the factors and interactions which influence the mean bonding strength.

For this purpose, a significance level (α) of 1% was chosen. All factors and interactions lower than α are regarded to be statistically significant. The results of the reduced model are shown in Table 4. The software JMP 16 (SAS Institute GmbH, Heidelberg, Germany) was used for the analysis, modelling and visualisation of the 2^4 – FFD.

Table 4. Table for main effects, interaction effects and p-values.

	Factors and Interactions	p-value
1	T_{MI}	0.00000
2	$V * D * TO$	0.00006
3	$D * TO * T_{MI}$	0.00173
4	$D * TO$	0.00173
5	V	0.02152
6	$V * T_{MI}$	0.02152
7	$V * D$	0.08596
8	D	0.10136
9	$D * T_{MI}$	0.10136
10	$TO * T_{MI}$	0.16194
11	TO	0.16194
12	$V * TO$	0.48153

With the data in Fig. 4, a prediction model for the mean value of the maximum bonding strength (R_{max}) is described through the four factors: *V, D, TO,* T_{MI} and their interactions by Eq. 1.

$$\begin{aligned} R_{max} = &- 17.437 + 1.500 * V + 0.389 * D + 1.360 * TO \\ &+ 0.036 * T_{MI} - 0.093 * V * D \\ &- 0.189 * V * TO - 0.004 * V * T_{MI} \\ &- 0.067 * D * TO + 0.009 * D * T_{MI} \\ &+ 0.011 * TO * T_{MI} + 0.014 * V * D * TO \\ &- 0.001 * D * TO * T_{MI} \end{aligned} \tag{1}$$

It is important to note that the factors and interactions participating in the model cannot be reduced further. Those factors or interactions which do not meet the α criteria (5 to 12; Table 4) are part of the significant ones (1 to 4; Table 4).

Having identified the significant process parameters and the interactions among them, the next step is to determine the optimal parameter setting which will maximize the bonding strength by optimizing Eq. 1 (Table 5).

Table 5. Optimal process parameter settings for maximizing the bonding strength (R_{max}).

Factor	Level for maximum bonding strength (R_{max})
Speed in m/min	4
Distance in mm	20
Track offset in mm	1
Metal insert temperature in °C	240

The visualisation of the model by three-dimensional graphs (Figs. 5 and 6) allows the representation of the relationships of *V*, *D* and *TO* to the target variable: bonding strength. Using these graphs, the designer of hybrid components can easily select an appropriate parameter combination to meet a specific economical and manufacturing constraint on the interface bonding strength.

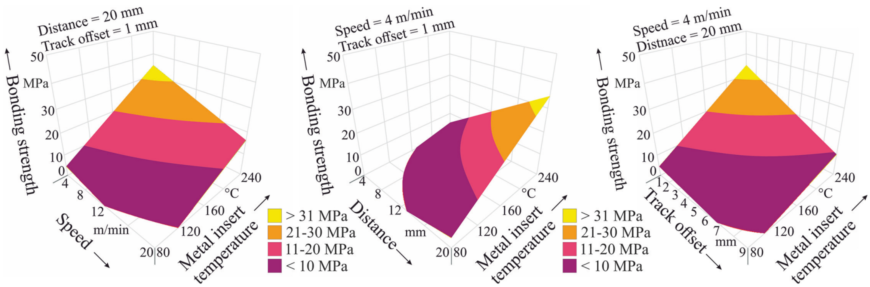

Fig. 5. Graphs representing the correlation between speed (left), distance (centre) and track offset (right) on the bonding strength in relation to the metal insert temperature.

If, for example, a high bonding strength is to be achieved by using infrared heating elements that limit the maximum preheating temperature to 160 ℃, Fig. 5 can be scanned for favourable settings of speed, distance and track offset. In this case the factor set of $D = 20$ mm, $TO = 1$ mm and $V = 4$ m/min leads to a mean bonding strength of 20 MPa. As the studies on induction assisted preheating [26] have shown, it is possible to achieve economic and consistent heating of complex shaped metal structures. Therefor the graphs in Fig. 6 are used to obtain convenient process parameters for fixed metal insert temperature.

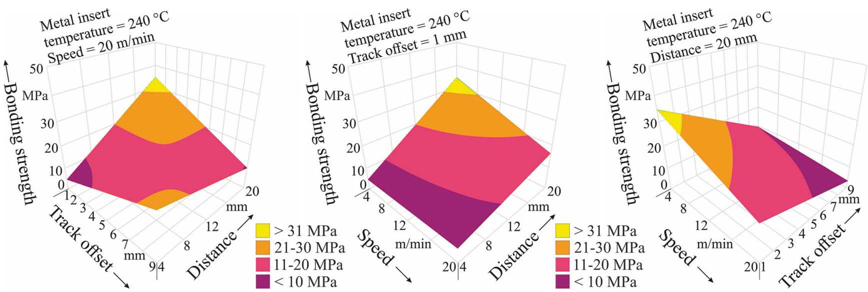

Fig. 6. Graphs representing the correlation between track offset (left), speed (centre) in relation to the distance and speed (right) in relation to the track offset on the bonding strength.

4 Conclusion

The precursor-based adhesion promoter applied by means of plasma technology enables a strong bond between metal and injection moulding compound. The application of the adhesion promoter is controlled by different process parameters leading to different bonding strengths. The metal insert temperature and the interactions of $V*D*TO$, $D*TO*T_{MI}$ and $D*TO$ have an increasing effect on the interface strength (Table 4). The determined bonding strength prediction model provides reliable results above 40 MPa.

Based on the model, the process and geometrical restrictions, the designer can estimate the bonding strength between the metal and injection moulding compound.

For the investigations of the process-structure-property relationship and the design of the model, only 4 of 81 possible process influencing factors are investigated in detail by full factorial design of experiments. There is still a need for further research, especially to investigate the influences of physical plasma generation and precursor chemistry on bonding strength to different metals and injection moulding compounds.

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Conflict of Interest

The authors declare that they have no conflict of interest.

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