Effect of new adhesion promoter and mechanical interlocking on bonding strength in metal-polymer composites

A Schuberth¹, M Göring², T Lindner¹, G Töberling¹, M Puschmann³, F Riedel¹, I Scharf³, K Schreiter³, S Spange³ and T Lampke¹

¹Materials and Surface Engineering Group, Institute of Materials Science and Engineering, Technische Universität Chemnitz, 09125 Chemnitz, Germany alexandra.schuberth@mb.tu-chemnitz.de
²Polymer Chemistry, Technische Universität Chemnitz, 09111 Chemnitz, Germany stefan.spange@chemie.tu-chemnitz.de
³Department of Joining and assembling, Fraunhofer Institute for Machine Tools and Forming Technology IWU, 09126 Chemnitz, Germany gerd.toeberling@iwu.fraunhofer.de

Abstract There are various opportunities to improve the adhesion between polymer and metal in metal-plastic composites. The addition of a bonding agent which reacts with both joining components at the interfaces of the composite can enhance the bonding strength. An alternative method for the adjustment of interfaces in metal-plastic composites is the specific surface structuring of the joining partners in order to exploit the mechanical interlock effect. In this study the potential of using an adhesion promoter based on twin polymerization for metal-plastic composites in combination with different methods of mechanical surface treatment is evaluated by using the tensile shear test. It is shown that the new adhesion promoter has a major effect when applied on smooth metal surfaces. A combination of both mechanical and chemical surface treatment of the metal part is mostly just as effective as the application of only one of these surface treatment methods.

1. Introduction

The reduction of the construction weight due to an increasing demand for resource and energy efficiency necessitates further development of metal-plastic composites as substitution for steel for automotive application. Fiber-reinforced plastics (FRPs) with their high stiffness and strength, corrosion resistance and various fabrication technologies [1] are appropriate for the manufacturing of FRP-metal hybrid components. Beside FRPs aluminum alloys can replace steel as metallic part for a further reduction of the construction weight.

For manufacturing metal-plastic composites with high mechanical load capacity, the adjustment of interface properties is necessary. This is because the joined materials exhibit strongly differing chemical and physical properties. Therefore, a chain entanglement effect as observed in polymer joints does not occur [2]. Nevertheless, the final joint strength of such composites can be improved by using a bonding agent. In this case, according to the chemisorption theory, the bonding can be caused by the generation of chemical bonds between the adhesion promoter and both of the joined parts. The mechanical theory of adhesion states that the topography and roughness of adhered surfaces correlate with the measured bonding strength. Depending on the viscosity and surface tension of the adhesive, it can penetrate pores and fill surface hollows of the joined parts. After the curing of the adhesive, a positive connection between adhesive and adherend is created [3]. The main aim of this study is to investigate the interaction of both adhesion mechanisms in connection with a new adhesion promoter.

2. Materials and surface treatment methods

2.1. Joining components
A glass-fiber-reinforced polyamide 6 (2-layered, bi-directional reinforcement) with a thickness of 2 mm was used in this study as plastic joining partner. As metallic components, two different bulk materials with a thickness of 1 mm were tested. In a prior investigation [4], the effect of the new bonding agent, produced by twin polymerization, was already approved for the system aluminum alloy – FRP. In this study, an additional aluminum alloy EN AW 6016-T4 (AlSi1.2Mg0.4) and steel DC06 were tested as references.

2.2. Adhesion promoter
The adhesion of a polymer to metals can be significantly improved by applying certain twin monomers (TMs) to the adherent surface [4]. Specific TMs offer the possibility that various functional groups can be introduced by a modular approach. In this work, a primary amino group was used inspired by well-known primer systems such as aminopropyltrimethoxysilane [5,6] or dendrimers. The introduction of amino groups is beneficial in so far as reactions with the carbonic acid end groups of the polyamide component and acid-base interactions with the metallic component surface are possible. Furthermore, the formation of silica will also lead to an improved bonding with the metal surface. The TMs used were synthesized based on commercially available reactants. TM (I) 2,2’-spirobi-[4H-1,3,2-benzodioxasiline] and TM (II) 2-(3-amino-n-propyl)-2-methyl-4H-1,3,2-benzodioxasiline were synthesized according to the literaure [7–9]. In a first step, TM (I) and TM (II), with a molar ratio of 15 to 85 [4], were pre-polymerized at 100 °C. The advantage is that the pre-polymerization is a good tool to control the reactivity, sensitivity and solubility of the adhesion promoter system. A 10 wt. % solution of the pre-polymer was prepared in ethanol for coating procedures. The solution was dropped on the metal surface via a syringe, and the volume dropped was approximately 0.15 ml per cm² of the metal surface area. The simultaneous twin polymerization of TM (I) and TM (II), which was performed at 180 °C, leads to nanostructured hybrid materials consisting of SiO2/poly-(3-aminopropylmethylsiloxane) and phenolic resin (Fig. 1). The adhesion layer is generated in a single process step.

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\begin{align*}
&\text{TM(I)} + \text{TM(II)} \xrightarrow{\Delta} \text{SiO}_2/n \text{SiO}_2/\text{NH}_2
\end{align*}
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*Figure 1. Simultaneous twin polymerization of monomer (I) and (II)*

2.3. Surface treatment
2.3.1. Grit blasting
Grit blasting is a widespread method for surface treatment, which provides surface roughening to various extents depending on the grit size and blasting parameters such as pressure, angle, and process time [10]. For this investigation, blasting was conducted with corundum FK-24 with a blasting angle of about 60°. The surface roughness is significantly increased by grit blasting with corundum. The bonding strength of the composite is improved by the mechanical interlock effect between plastic and metal [10].

2.3.2. Laser structuring
Laser structuring is an innovative surface treatment method based on conventional laser ablation, which can be used to create fine structures at nano- and micro-scale level on the metallic surface. A wide variety of treatable materials and producible structures, no machine wear because of non-tactile machining, short processing times as well as low-level, localized laser energy input to the component are the main advantages of this technology. Due to the low energy input and fast beam guiding, laser structuring is suited for the treatment of localized zones and temperature sensitive component parts [11]. In the course of laser structuring, a laser beam is focused on the surface of the parts being machined. In so doing, high temperature and evaporation pressure are induced, ejecting the molten and partially vaporized material from the surface. As a consequence of the melt solidification at the edge of formed cavities and above the metallic sheet surface, undercut structures can be produced. These undercuts
provide a good possibility for the clamping of reinforcing fibers and polymer matrix material of FRPs during the manufacture of metal-plastic composites [11]. The geometrical shape (depth and width) and dimensions of surface structures depend on the material properties and process parameters such as laser power, pulse duration, feed rate, and number of run. For example, excessive energy input during the treatment of materials with low-viscosity melts may affect or reclose already formed structures by increased spattering. Hence, no capacity for mechanical interlocking will be produced. Therefore, the parameter sets for the surface treatment of aluminum and steel have to be adapted to each specific material.

The laser structuring of the test samples was performed at the laser machining center Orca-μ (Acsys Lasertechnik GmbH). As a beam source, a pulsed fiber laser with maximal power of 20 W and wavelength of 1070 nm from IPG was used.

In order to avoid the above-mentioned welding of the formed cavities during the treatment of the aluminum surface, a laser power of about 13–14 W was used and the number of laser runs was reduced to one. When surface structuring the steel samples, it was found that a multiple treatment results in a significant increase in structure depth with a simultaneous increase of the bulging height above the sheet surface. In contrast to aluminum, no welding or reclosures of cavities were observed. For the treatment of steel, a laser power of 18 W was applied and the number of laser runs increased to 10.

2.3.3. Thermal spray coating
Thermal spray coating is a conventional method for application of coatings on various substrate materials with relatively low deformation. During this process, the coating material is fed to a torch most commonly in form of powder or wire and usually heated close to or above its melting point. The molten or softened particles of the feed-stock material produced this way are accelerated by a gas or plasma stream and applied onto a substrate. During the impact on the substrate, the droplets are deformed and solidified [12]. Depending on the particle size and process parameters, the surface roughness and open porosity can be adjusted in order to generate surface cavities and undercuts, which can be exploited for mechanical interlocking. Particularly arc spraying is capable of generating high surface roughness due to its characteristically broad particle size distribution. The Visu Arc 350 arc spray system was used for applying a coating on aluminum. As feedstock material, a cored wire of NiAl 95/5 (1.6 mm thickness) was chosen for this study, which is typically applied as bonding layer beneath ceramic coatings to enhance adhesion to the substrate. The current and voltage of the arc were 150 A and 30 V respectively. The distance between the spraying gun and aluminum substrate surface was 130 mm.

3. Characterization methods
The shear tension test according to DIN EN 1465 was used to evaluate the effectiveness of the twin polymer as well as the various techniques of mechanical surface structuring individually and in combination with each other. The metal and plastic parts were bonded by thermal joining at an elevated temperature (350 °C for aluminum and 400 °C for steel). When the required joining temperature was attained, the bonding force of 250 N was applied and the sample was cooled by compressed air under constant load. The overlapping length was selected to be 5 mm in order to avoid plastic deformation of thin metallic joined parts during the mechanical test. The shear tension test was carried out at room temperature and at a strain rate of 1 mm/min. A universal testing machine (Zwick AllroundLine Z020-20 kN) was used for these tests. The maximum tensile force was measured and the bonding strength was calculated. At least five tests were carried out for each interface design. Prior to the application of the adhesion promoter, the surface topography of the metallic part after the surface structuring treatment was investigated by means of an optical three-dimensional profilometer (3D profilometer, GFMesstechnik GmbH).

4. Results and discussion
The images depicted in Table 1 were recorded by a non-contact optical 3D-profilometer. They show the surface topography of metallic samples (4 mm x 3 mm) after different treatments prior to the joining with the plastic part. Due to the different hardness levels of the used metallic materials, the resulting surface roughness Ra of the grit-blasted aluminum samples is higher than that of similarly treated steel.
samples. Thermally sprayed coatings of NiAl 95/5 on both substrates show no significant difference. The laser-structured surface of the steel sheets exhibits much deeper cavities and much higher bulging compared to the aluminum sheets because of multiply repeated laser treatment, as discussed in 2.3.2.

### Table 1. Surface topography of metallic parts after different treatments.

| Treatment                      | Steel Ra | Aluminum Ra |
|--------------------------------|----------|-------------|
| Grit-blasted                   | 10.2 µm  | 7.3 µm      |
| Thermally sprayed NiAl 95/5    | 7.5 µm   | 8.4 µm      |
| Laser-structured               | 9.5 µm   | 3.4 µm      |

The results of the shear tension test confirm the effect of the adhesion promoter produced by twin polymerization, as was already observed in previous investigations with pull-off tests [4]. The developed bonding agent has also a major effect as an adhesion promoter for the joining of steel with FRPs. By applying this adhesion promoter to an unstructured, untreated metallic surface, it is possible to increase the bonding strength of metal-plastic composites by the factor of 7 to 10 (Figs. 2 and 3). Mechanical surface treatments of metallic parts without the application of an adhesion promoter also lead to a significant enhancement of the resulting bonding strength in comparison to untreated metallic parts. Only grit blasting is less effective than the chemical treatment with the novel bonding agent, as it was already discussed in [4].

Not only the surface roughness, but also more complex aspects of the surface topography determine the mechanical interlocking effect when joining different materials [13]. Grit-blasted surfaces offer less anchorage points for mechanical interlocking compared to thermal sprayed surfaces with open porosity or laser-structured surfaces with deep grooves and high bulging. As a consequence of this, the bonding strength of samples with a grit-blasted metallic part is lower than those with a thermally sprayed or laser-structured metallic part. The highest values of the bonding strength, which were determined by testing samples with solely mechanically treated metallic parts, are about 23–25 MPa for both metals investigated.
Generally, the application of an adhesion promoter on the surface-structured samples exhibited no improvement of the results. This indicates that no closed homogeneous film of the adhesion promoter was formed on the structured metallic surface, possibly due to poor wettability of the metallic surfaces or deficient viscosity of the adhesion promoter. The only marked exception to this was observed for grit-blasted steel surfaces. Here, the resulting bonding strength exceeds 25 MPa. The determining mechanism should be investigated in detail. In addition, the influence of prepolymerization parameters, quantity as well as the application method of the applied adhesion promoter are subject to further investigation.

Nestler et al. [13] used chemically and mechanically differently treated aluminum in their study on aluminum–FRP joints. They found that the application of an adhesion promoter based on twin polymerization or grit blasting of metallic part results in similar average bonding strengths of 15–16 MPa. Lower bonding strengths, compared to the results presented here, may be caused by different joining parameters, used materials and the sample geometry. The maximum bonding strength of 17–19 MPa was achieved in [13] by using chemical pretreatments like etching or anodizing or by the application of a thermally sprayed coating. Therefore, it should be investigated whether a chemical pretreatment could be advantageous in combination with the newly developed adhesion promoter.

5. Summary and Conclusion
In this study, the separate and combined effect of an adhesion promoter produced by twin polymerization and structured metallic surfaces on the tensile shear strength of metal-polymer composites was investigated. The novel chemical bonding agent caused a significant increase of the bonding strength of metal-plastic composites, particularly when using aluminum as the metallic part. A surface-structuring pretreatment of the metallic part by thermal spraying or laser structuring resulted in higher bonding strength values. A combination of both types of surface treatment was generally not more effective than the individual surface treatments. Hence, the surface treatment method should be adjusted with regard to the practical application of metal-plastic composites, the dimension and shapes of individual composite parts.

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