Even Aluminum Can Not Resist

Further Development of the Plasma-SealTight Process and Materials for Chemically Bonded Plastic-Metal Hybrids

Bonding plastic to metal is an effective means of achieving economic lightweight construction with high functional integration. In this process, media-tightness is a key criterion for the quality of the bond. Deposition of a plasma layer combined with customized modification of the plastic give rise to extremely strong hybrid components.

The joint between metal and plastic in an injection molding process can either be achieved by a mechanical connection or a chemical bond. A mechanical connection can be produced directly in the injection mold through undercuts for example. This is a purely mechanical fixation of the plastic component in the metal. To produce chemical bonds, conventional adhesion promoter systems are used. The metal is pretreated with adhesion promoters to enable a bond to different plastics.

The purely mechanical hybrid joint often fails to meet the service life and strength requirements demanded of the actual part. Due to capillary effects, moisture or other media can penetrate the interface between the plastic and metal. This media ingress leads to corrosion, cracking and ultimately to separation of the plastic component from the metal.

A chemical bond, in which the plastic is chemically bonded to the metal at molecular level, requires the use of solvent-based adhesion promoters and primers. In many cases, these promoters are applied to the metal surface in a wet-chemical process involving costly and environmentally harmful chemicals.

In the Plasma-SealTight process, after prior inline plasma cleaning, the strengths achieved are such that the metal component of a lap shear test specimen fails before the hybrid bond. Unlike with steel, in the case of aluminum, the oxide layer must be removed first (© Akro-Plastic).
The limitations of such processes, as described above, prevent their widespread use in industry. Thus, there is a need for a changed process to obtain a chemical bond between plastic and metal surfaces using adhesion-promoting layers.

Addressing this need, Akro-Plastic GmbH, Niederzissen, Germany, and Plasmatreat GmbH, Steinhagen, Germany, embarked on a collaborative project to develop an inline process to obtain a chemical bond between plastics and metal surfaces via adhesion-promoting layers. In the course of this partnership, an ultra-strong, media-tight hybrid bond was developed through the combination of Plasma-SealTight technology (PST) and adhesion-modified polyamides from Akro-Plastic (see *Kunststoffe international* 6-7/2016, p. 8). In this process, adhesion promoter systems are applied to the metal using a dry-chemical method. Such a plastic-metal bond has good long-term stability, is weather-resistant, and withstands temperature variations. With the PST process, far higher tensile shear strength values can be achieved than with currently established processes (Fig. 1). Furthermore, the PST process can be used inline and ensures a high degree of flexibility and automation.

**The Plasma-SealTight Process**

The PST process is a cleaning and coating technology based on the use of atmospheric pressure plasma (Openair plasma). The coating system consists of a generator, transformer, and plasma nozzle. Inside the nozzle, a pulsed, arc-like discharge is created in the stream of process gas. This results in partial conversion of the process gas into the fourth state of matter: plasma.

In the first stage of the PST process, the surface of the metal is cleaned with Openair plasma. In the second stage, an adhesion-promoting layer is applied through a PlasmaPlus nozzle. Through the high-energy excitation in the plasma, the adhesion promoter (precursor) is fragmented. Together with the plasma, the excited and fragmented precursor is deposited onto the metal and reacts with the metal surface. This produces a layer with completely new properties. Depending on the precursor used, the layer may have a different chemical structure and can be tailored to specific application requirements. The final process stages involve heating the metal component and overmolding it in the injection molding process.

The chemical structure of the precursor, coating parameters, the plastics compound and the temperature of the metal during overmolding influence the quality of the plastic-metal bond. To investigate the different factors influencing bond strength, Akro-Plastic has installed a complete production cell for hybrid components at its Niederzissen site, consisting of an injection molding machine (type: Sytec 100/420-310, manufacturer: Sumitomo (SHI) Demag), a turnkey PST cell (type: PTU1212/PAD, manufacturer: Plasmatreat), and two handling robots (type: KR 6 R900 sixx, manufacturer: Kuka). The trials currently being conducted aim to develop compounds customized for different metal-plastic combinations, which can then be supplied as proved and tested system solutions.

Besides cleaning and coating the metal, the injection molding process is also very important for the quality of the plastic-metal bond. When the metal insert had been positioned in the mold, it must be heated in the PST process to a temperature above the melting point of the thermoplastic. Controlling the temperature of the metal insert during injection of the thermoplastic melt into the cavity is a key requirement and has a major influence on the mechanical strength of the bond. In order to control the temperature of the metal insert an induction heating system was integrated into...
the existing mold to allow for inline heating of the metal insert.

**Adhesion-Modified Compounds Based on PA6**

The trials are focusing particularly on the adhesive bond between stainless steel 1.4301 and an adhesion-modified polyamide 6 reinforced with 30% glass fibers (Akromid B3 GF 30 1 PST (6647)). Adhesion is evaluated using lap shear specimens as per DIN EN 1465. Thus, the strength of any metal-plastic combination can be determined with a standardized test specimen.

The tensile shear strength of the hybrid made out of stainless steel 1.4301 and PA6 compound Akromid B3 GF 30 1 PST (6647) reaches 50 MPa according to the most recent trials. With a standard commercially available polyamide 6-GF30, a tensile shear strength of 30 MPa is obtained under the same manufacturing and test conditions. Besides stainless steel, other metals have also been tested in bonds with Akromid B3 GF 30 1 PST (6647) (Fig. 2).

Stresses induced by thermal cycling weaken the hybrid structure of conventionally made plastic-metal bonds. With the PST process and adhesion-modified polyamides, a significant advance has now been achieved. The tensile shear strength of a hybrid made out of stainless steel (1.4301) and an adhesion-modified polyamide compound after thermal cycling from -40°C to +150°C was still at 85% of its original value (Fig. 3). Similar behavior can be observed after heat aging in air at +150°C for 5000 h. It can be shown that the hybrid bond still retains 86% of its original strength (Fig. 4). By comparison, the mechanical strength of only the plastic under the same storage conditions drops to 77% of its initial strength.

![Fig. 3. Effect of thermal cycling on the metal-plastic bond strength of Akromid B3 GF 30 1 PST black (6647) and stainless steel 1.4301 (source: Akro-Plastic)](image-url)
The boundary layer between the two materials has been a risk factor so far. In a plastic-metal bond, the boundary layer is vulnerable to the ingress of ambient media without special sealing. To prove the media tightness of a PST bond a bubble test using a high-voltage plug as a demonstrator was preformed. The material combination consisted of copper overmolded with PPA-I-GF35.

The PST process proved superior to other technologies, such as labyrinth sealing or laser-structured surfaces. The components withstood 200 thermal cycles from -30°C to +180°C over a cycle time of 80 min. After 50 test cycles, the plugs were immersed in a water bath and subjected to compressed air at an excess pressure of 0.5 bar for 60 s. The next best process was laser structuring, where the components withstood on average only 125 cycles.

**Aluminum as First-Choice Metal Partner**

To fully exploit the lightweight construction potential of plastic-metal hybrids, the use of aluminum as the metal partner to the plastic is essential. The special challenge with aluminum is to remove the oxide layer, which prevents formation of a strong hybrid bond. In the PST process, controlled removal of the oxide layer by Openair plasma during the first cleaning stage has been successfully achieved (Fig. 5). The tensile shear strength of a hybrid consisting of aluminum (Al 6061) and PA6-GF30 (adhesion-modified), achieves a level of 35 MPa. In many of the tensile shear tests, the aluminum fails before the adhesive bond (Title figure). Cleaning and coating parameters for the metal alloys shown in Figure 2 were determined through systematic variation. The formulation of a compound can influence bond strength positively as well as negatively. The same can be said for the processing window in the injection molding process. For optimum results, it is essential to map both homogeneous heating of the metal inserts as well as the temperature during overmolding for serial production. Consequently, Akro-Plastic and Plasmatreat have been collaborating with experts in their respective fields since the beginning of 2018. For heating the metal inserts, Cobes GmbH, Weisweil, Germany, has been providing support in terms of equipment and advice. This company specializes in target-ed induction heating of electrically conductive materials such as metals or CFRP. Kegelmann Technik GmbH, Rodgau-Jügesheim, Germany, has expertise in mold-making and 2-component hybrid production for prototypes and small lots. This company is helping to implement new mold concepts and integrate heating technology into the injection mold.

**Implementation of Serial-Production Applications**

Through the partnership between Plasmatreat and Akro-Plastic and cooperation with various companies across the entire value chain, the process described is being continually developed and transitioned into serial-production. The chemically bonded plastic-metal combinations created with this process offer improved solutions for economic and automated production of hybrid components compared to established processes.

A new project with K.A. Schmersal GmbH & Co. KG, Wuppertal, Germany, will be introduced in 2019. The Schmersal Group is active as a system and solution provider in the area of safety switchgear for personal and machine protection.