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DICHTUNGS TECHNIK

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ISGATEC®

No chance for corrosion

AP plasma enables tight hybrid bonds

The migration of moisture in combination with oxygen at the interface of an injection molded plastic-to-metal joint can lead to corrosion and premature adhesive failure of the hybrid component. An atmospheric plasma sealing technology combined with application-specific thermoplastic compounds promises to combat this issue in the long term.

Practical experience shows that even an injection-molded bond that was originally tight can become untight over time, lose cohesion and often lead to the functional failure of the components. If not properly sealed, the plastic-metal interface provides a permanent pathway for the ingress of water, air or other media.

Various companies and research institutes have long been exploring how to minimize this risk or eliminate it altogether. The plasma sealing technology Plasma-SealTight (PST) offers a new approach to ensuring a very strong, media-resistant hybrid bond (Fig. 1). The composition of a plasma-polymerized layer generated under atmospheric pressure, the recipe for the plastic compound and the process parameters are precisely matched to create a long-time stable, media-tight bond of the injection-molded part.

Plasma coating under normal pressure

The new plasma sealing process is based on the atmospheric PlasmaPlus technology developed and patented over ten years ago. This discovery made it possible to produce functional thin-film coatings for the first time under atmospheric pressure – dispensing with the costly separate vacuum chamber needed for low-pressure applications – and to apply plasma polymerization coatings in continuous production.

Plasma-SealTight is a dry, environmentally friendly process. It replaces the wet-chemical cleaning and priming steps frequently used to pretreat hybrid injection-molded components and is both reliable and reproducible. It also entirely eliminates the need for process steps such as drying or intermediate storage, since components can be

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further processed inline immediately after coating.

Multi-functional with millimeter precision

When creating an interfacial layer between two dissimilar materials, the principal challenge for developers is to ensure that its chemical properties achieve simultaneous bonding between two different materials. The task becomes even more complex if the materials belong to different groups, as is the case here with metal and plastic. Water or other media can easily penetrate the interface and spread across the surface of materials that do not have a chemically bonded connection. The PST seal prevents this effect by filling the microscopic cavities like a fine mist, bonding to the metal surface and forming a corrosion-proof barrier (Fig. 2).



Fig. 1: The chemical-physical Plasma-SealTight process enables the area-selective deposition of functional nanocoatings in milliseconds and thus the creation of covalent bonds between different materials

(Photo: Plasmatrete GmbH)

Plasma-SealTight is a chemical-physical process that creates a covalent bond between different materials by means of layer deposition in atmospheric pressure plasma. The layer bonds with the metal at molecular level and forms such a strong adhesive bond and tight seal with the modified plastic compounds that in addition it takes on the function of an anticorrosive coating.

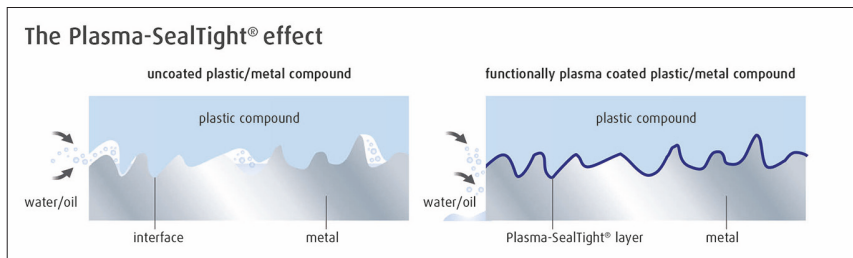


Fig. 2: If water or other media penetrate the interface of the plastic-to-metal bond, it can lead to corrosion, failure of the component function or even delamination (left). The plasma polymer layer (right) fills every cavity, leaving the water no opportunity to penetrate the interface

(Photo: Plasmatrete GmbH)



Fig. 3: The metal body (left) can be overmolded with the thermoplastic compound (right) immediately after atmospheric pressure plasma coating to produce a strong joint

(Photo: Plasmatrete GmbH)

A precursor in the form of an organosilicon compound is added to the plasma to produce a coating. High-energy excitation within the plasma fragments this compound and deposits it on the surface in the form of a vitreous coating. The chemical composition can be varied according to the application to ensure that optimum functionalization is obtained for any given material. A further advantage of the process is its great flexibility. In particular, the coating thickness and process speed can be precisely matched to a specific application. Without doubt, the special advantage of this process over other coating techniques is the fact that layer deposition is area-selective, i.e. the nozzle technology enables it to be targeted

with pinpoint accuracy to a precisely defined location, even at very high processing speeds. A 100 nm thin coating is deposited in milliseconds, whereas it would take around one to two minutes to do this using low-pressure plasma (vacuum chamber) and localized selection would not be an option.

By developing new precursors and extensively adapting the plasma parameters, the developers of the PST process have succeeded in selectively incorporating several functions into a single layer. These functions include good bonding to the metal surface, enhanced corrosion resistance, acting as a media and oxidation barrier and adhesion-promoting properties for plastics through the creation of functional chemical groups. Whilst the silicon contained in the layer facilitates adhesion to metal and metal oxide, silicon oxide is responsible for the barrier effect and media tightness. The organic components in the layer (functional groups) form the adhesive bond with the polymer.

Tailor-made plastic recipe

When formulating recipes for their plastics, manufacturers have to take into account many characteristics of the subsequent product specified by the customer – mechanical, electrical, thermal and chemical properties, the plastic's fire rating and general properties such as density and moisture absorption. Each plastic matrix is modified

through the addition of additives, fillers and reinforcing materials. It is these recipe components that turn a base plastic into an application-specific plastic compound.

To guarantee consistent product quality and thus the functioning of subsequent components, the manufacturer must have an extremely precise and reproducible compounding process. The compound was manufactured by a company that specializes in complex, customized adaptations of plastic properties. Having developed its own compounding technology, this company can satisfy the above-mentioned requirements for functional integrity and quality internationally, regardless of the production location. So it was tasked with creating a compound with specific properties for the project. The chemical recipe had to take account of two main aspects – the different coefficients of linear expansion of plastic and metal on the one hand, and the chemical-physical adhesive bond with the plasma polymer layer on the other. When all the criteria have been evaluated and adjusted, the atmospheric pressure plasma-coated metal can be overmolded immediately with the thermoplastic compound to produce a strong bond without the need for any additional resources or measures (Fig. 3).

Double the adhesive strength

In the current validation phase for customer-specific projects, the system partners are focusing on glass fiber-reinforced plastics for the base compound which are modified as testing progresses. The test specimens mainly consist of aluminum, steel and stainless steel each overmolded with PA6 GF30 or PA66 GF30 thermoplastics. The results of the adhesion tests are convincing: Steel test specimens treated with Plasma-Seal-Tight achieve tensile shear strengths on average twice as high as those specimens which undergo laser structuring or to which an adhesion-promoting primer is applied in an effort to produce a long-time stable metal-to-plastic bond (Fig. 4).

The functionality of the plasma layer is continuously optimized – in terms of both adhesion and anti-corrosion protection. The aim of the subsequent corrosion resistance tests was to discover the extent to which artificial aging weakens the required bond strength. Hybrid test specimens consisting of aluminum and stainless steel combined with a thermoplastic PA6 GF30 underwent a one-year accelerated weathering test (as per DIN 55665), after which the tensile shear strengths were found to have decreased by only around 20% (Fig. 5). This more or less corresponds to the decrease in tensile shear strength of the polymer in the unjoined state. All ongoing tests confirm the desired cohesive failure in the plastic for the metals aluminum and stainless steel (Fig. 6). Due to the high level of interest shown by the plastics processing industry in this process, in 2017 the system partners decided to establish a joint tech-

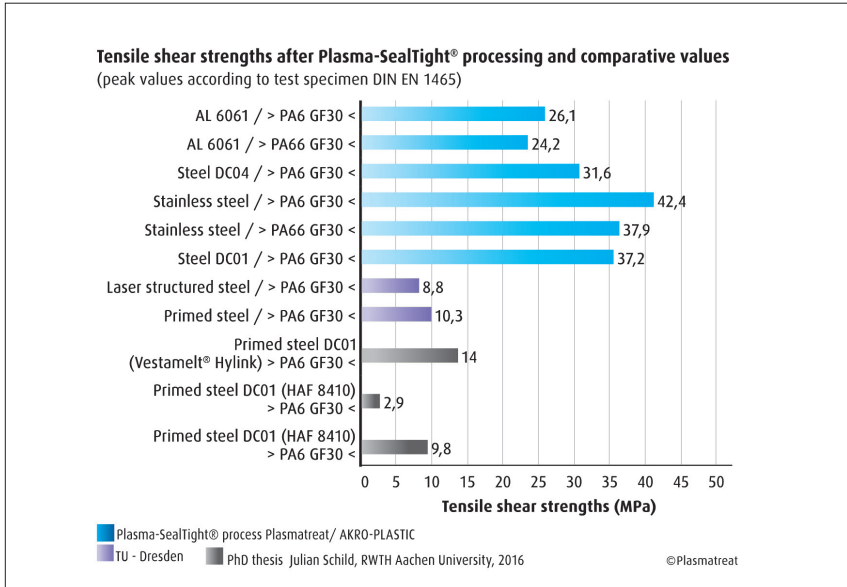


Fig. 4: Comparison: The achieved maximum tensile shear strengths of Plasma-SealTight bonds far exceed those of test specimens coated with adhesion promoter or laser-structured test specimens (Photo: Plasmatreat GmbH)

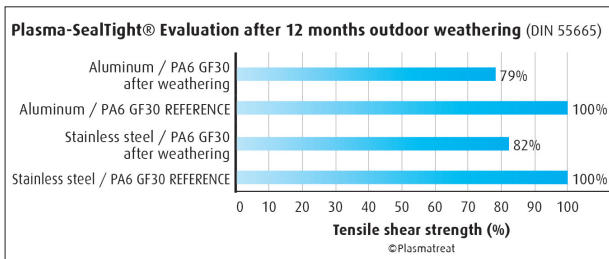


Fig. 5: Test results: The tensile-shear strengths of the plasma-sealed hybrid test specimens decreased by only around 20% after outdoor exposure for one year (Photo: Plasmatreat GmbH)

nology center for Plasma-SealTight. This center houses a plasma pretreatment and coatings unit developed in-house specifically for this process. Tests conducted here on behalf of customers involve a large number of other material combinations, including different metals, polyamides with varying glass fiber contents as well as other polymers such as PBT and PPA.

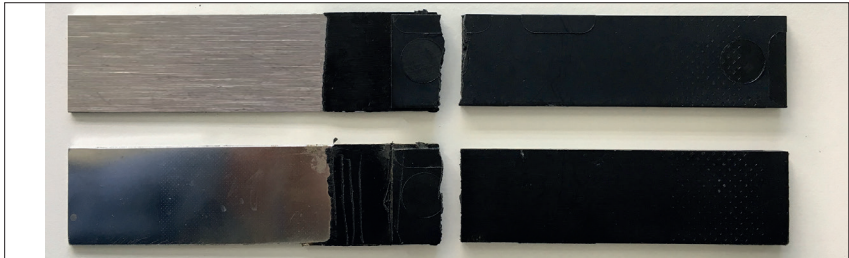


Fig. 6: Even after weathering for twelve months, the PST-coated aluminum and stainless steel test specimens achieved the desired cohesive fracture in the plastic (Photo: Akro-Plastic)

Media-tight seal

Tests on plasma-coated metals showed that the layer forms a barrier against water, saline solutions and gases and thus prevents the subsurface migration of these media. The polymer bonds to the metal by means of a chemical reaction, i.e. the bonding of reactive groups.

For example, a stainless steel test specimen was plasma-coated on one half only, fully overmolded with PA6 GF30 and then placed in a corrosive medium for several weeks. On removal, the plastic was mechanically removed and the metal was analyzed under a microscope. There was a clear distinction between the uncoated, now badly corroded area and the plasma-coated, corrosion-free metal surface (Fig. 7).

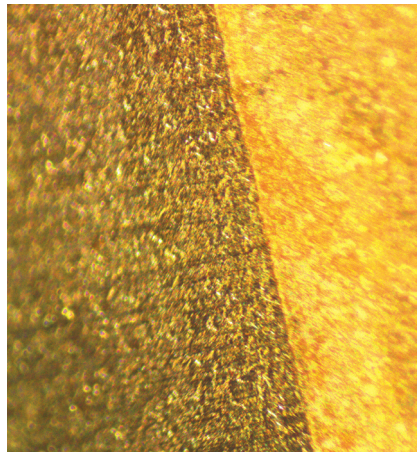


Fig. 7: The micrograph shows a clear distinction between the plasma-coated, corrosion-free metal surface (left) and the uncoated, corroded area (right)

(Photo: Plasmatreat)

A further series of tests was then carried out together with an automotive and industry supplier. One test involved comparing the PST process with other technologies on the market. Cyclic climatic testing and bubble leak tests were conducted to demonstrate the tightness of a hybrid test specimen plug-in connector under water. The metal/plastic material combination consisted of copper (blank) overmolded with a PPA-I GF30 plastic compound (impact-modified polyphthalamide with 30% glass fiber) (Fig. 8). The development team chose to compare a standard copper plug-in contact

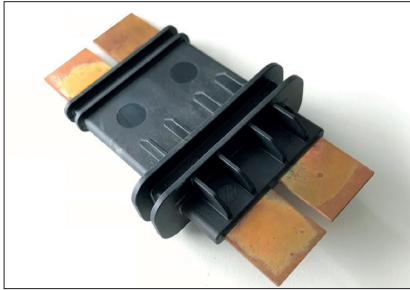


Fig. 8: The bubble leak test was performed on a prototype comprising copper (blank) overmolded with a PPA-I GF30 plastic compound (Photo: Schaeffler Technologies)

without any pretreatment as a reference, and the three sealing technologies labyrinth structure, heat-shrink sleeve and laser structuring with the Plasma-Seal-Tight process.

For the bubble test, the test specimen was mounted in a connection adapter, which was pressurized with air at one end to a predefined test pressure, while the other end was immersed in a liquid test media under positive pressure. With this test, rising bubbles indicate a possible leak in the hybrid bond, in other

words, insufficient media-tightness. All test specimens were put through this test for the first time immediately after manufacturing in the injection molding process. Then the cyclic climatic testing was performed at a temperature range of -40 °C to $+180\text{ °C}$ in a total of 200 cycles. After every 50 cycles, the components were removed from the test chamber and retested under water. The results showed that the components joined using the plasma sealing technology achieved significantly better tightness values than the comparative methods (Fig. 9).

Technical implementation

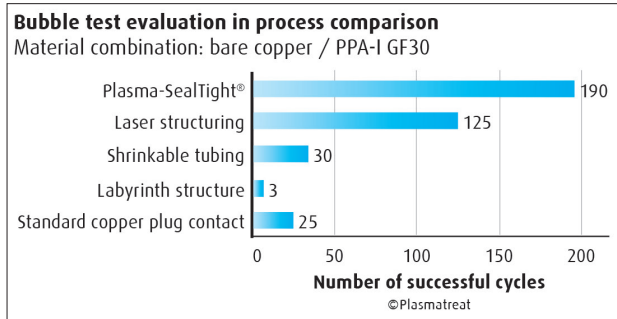
The turnkey, fully automated PTU1212 plasma cell was developed to enable shop floor implementation of the Plasma-SealTight technology Fig. 10. The cell, which can be adapted to suit any conventional injection molding machine, makes the process faster and at the same time allows for the continuous flow production of mass-produced plastic-to-metal components. It contains everything the pretreatment process needs, from the generator, robot, control technology, plasma control unit (PCU) and plasma jets to cables and consumables. The plasma system itself has two separate plasma nozzles. A robot – or with the two smaller variants, an XY axis system – guides the metal inlay initially beneath the Openair plasma beam, which removes any contamination from its surface at molecular level, thus restoring its original good wetting behavior. The functional coating is applied immediately afterwards from the second plasma nozzle.

Summary

The new plasma sealing process offers a pioneering solution for improving plastic-to-metal bonds in the injection molding industry. The system partnership between the

Fig. 9: The Plasma-SealTight process produced the best sealing performance in the technology comparison

(Photo: Plasmatrete GmbH)



two specialists provides users with a particularly high degree of security for customized requirements. According to data from the manufacturers, the new process ensures greater product quality in addition to a reliable, reproducible and cost-effective production process, whilst at the same time being completely environmentally benign. All in all, the Plasma-SealTight process offers a host of benefits:

- In-line use in the injection molding production line (no external transport routes) reduces costs and provides an industry solution that can be used globally.
- Reliable, reproducible process with high development potential (new material combinations) and area-selective pretreatment at very high speeds
- Component quality increased by significantly improved bond adhesion, corrosion protection of metal inserts, media-tight interface and consistent product quality ensured by high precision and reproducibility of the compounding process.
- Environmental protection/sustainability by completely eliminating the use of solvents, primers, acids, no VOC emissions, very minimal use of chemicals (precursors), high energy efficiency due to low energy consumption of the plasma unit and elimination of transport routes and drying processes for semi-finished parts.



Fig. 10: The turnkey, fully automated PTU1212 plasma cell contains everything the plasma process needs and can be connected to any conventional injection molding machine

(Photo: Plasmatrete GmbH)