SPECIAL:
HYBRID PROCESSES AND MATERIAL CONCEPTS

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Ultra-Strong and Media-Tight

Atmospheric Plasma Coating Ensures Plastic-to-Metal Bonds in the Injection Molding Process

After two years of preparation, a plasma specialist and a plastic compounds manufacturer have joined forces to launch a new systems solution on the market that not only promises a particularly strong, media-tight plastic-to-metal bond in the injection molding process, but is also corrosion-resistant, environmentally friendly and particularly cost-effective.

Water-tight: The atmospheric pressure plasma nozzle technology developed by Plasmatreat around 20 years ago can now be used to produce corrosion-resistant bonds for hybrid components (© Plasmatreat)

The bonding of thermoplastic compounds to metal is state-of-the-art in injection molding and used in many industrial applications. However, the interface where the completely different materials meet is still regarded as a risk factor. If not properly sealed, it provides a permanent pathway for the ingress of water, air or other media in a plastic-to-metal bond.

Practical experience shows that even an injection-molded bond that was originally tight can become untight over time, lose cohesion and ultimately lead to the functional failure of the components. In many cases premature adhesive failure is caused by the absorption of moisture in combination with oxygen, which results in subsurface migration at the interface. Water ingress in the boundary area leads to corrosion of the metal and in most cases to complete functional failure.

The industry therefore has an ongoing interest in new technologies which can outstrip existing ones not only in terms of ever-increasing performance and durability of hybrid parts, but also with regard to their efficiency and environmental compatibility. One such alternative now offers a new process which precisely matches the composition of a plasma polymer layer generated under atmospheric pressure to the recipe for the plastic compound and the process parameters to create a long-time stable, media-tight bond of the injection-molded part.

Plasma under Normal Pressure

Around 20 years ago Plasmatreat GmbH, Steinhagen, Germany, became the first company to integrate atmospheric pressure plasma into in-line production processes through the development of plastic nozzles. Prior to this, atmospheric plasma was hardly used in industry, but this breakthrough made its use under normal air conditions entirely feasible on an industrial scale

Fig. 1. The two project managers Leonhard Enneking from Plasmatreat (left) and Edgar Düvel from Akro-Plastic (right) established the system partnership between the two companies (© Plasmatreat)

Fig. 2. Atmospheric PlasmaPlus technology: The chemical-physical coating process enables the area-selective application of functional nanocoatings and the formation of covalent bonds between different materials (© Plasmatreat)

for the pretreatment, i.e. microfine cleaning and simultaneous activation of material surfaces. Alongside numerous other applications, the manufacturer uses this technology today to produce waterproof bonds for hybrid components (**Title figure**).

Following a period of intensive development, the plasma systems engineer achieved another first: A plasma coating generated under atmospheric pressure was used for the first time on an industrial scale. Up until this point, plasma thin-film processes could be produced only under low-pressure, i.e. in a separate vacuum chamber. PlasmaPlus, the technology developed and patented in partnership with the Fraunhofer Institute for Manufacturing Technology and Advanced Materials IFAM, Bre- »

Fig. 3. Mixed fracture under the microscope: Some of the glass fibers from the polyamide compound are firmly anchored in the plasma polymer layer (© Akro-Plastic)

men, Germany, marked a turning point. Now at last there was an opportunity to apply functional coatings to material surfaces in-line under completely normal production conditions. This environmentally friendly process makes many environmentally harmful processes – including the use of solvent-based adhesion promoters and primers – entirely redundant without any ensuing loss of quality.

Since PlasmaPlus was integrated into the production process at TRW Automotive in 2007, the bonded joints of die-cast aluminum motor pump housings have been coated with PlasmaPlus to prevent corrosion. On the basis of this success, Plasmatreat went on to invest in the research and development of plasma polymer coatings with other functions.

Vision and Challenge

Whilst the use of PlasmaPlus technology soon became standard for bonding and painting processes, its use in hybrid injection molding remained a vision until very recently. Leonhard Enneking, who for ten years has been 2-component specialist, key account manager and project manager at Plasmatreat, had long been seeking a suitable plastics manufacturer to form a system partnership with. The suitable candidate not only had to be willing to tackle this exciting topic with him in-depth, but would also have to be capable of implementing it rapidly into the production process at a later date. He found the right partner two years ago in Edgar Düvel, plastics engineer and key account manager at Akro-Plastic GmbH, Niederzissen, Rhineland-Palatinate, Germany. He was very interested in the idea of a joint systems solution and put it to his management board. The manufacturer, which specializes in plastic compounds, or more precisely in the application-based refinement of standard and technical plastics, welcomed the offer of collaboration with the plasma company in this market segment and named Edgar Düvel as Ennekings counterpart (**Fig. 1**).

Following preliminary trials, strategic market analysis was undertaken in the first year to explore the barriers to market entry and the most important topics for users. On the basis of this

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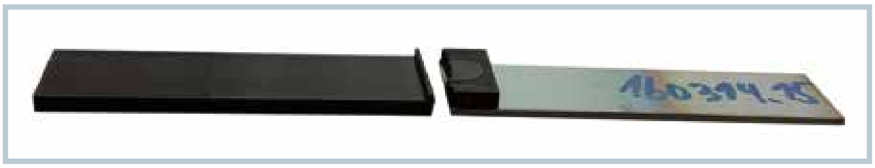

Fig. 4. Cohesive fracture of a PA6GF30-stainless steel test specimen bonded using the PlasmaPlus process (© Plasmatreat)

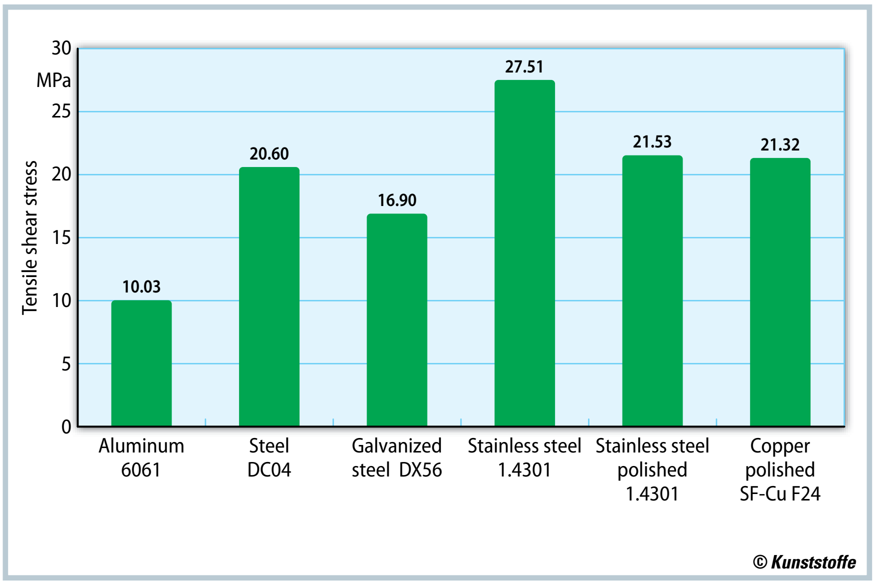

Fig. 5. After PlasmaPlus coating, the injection-molded hybrid part shows high tensile shear strengths for steel, stainless steel and copper (source: Plasmatreat)

analysis it was decided to focus initially on technical plastics in general and thermoplastics (polyamides) in particular, since these play an important part in most technically based industrial and automotive applications. "The challenge", says Enneking "was to develop a new functional coating on the one hand, and a complete industrial solution on the other". Achieving this goal required not only a stable process and suitable consumables; the chemical composition and processing properties of the new plasma coating also had to be reliable and ergonomic, i. e. user-friendly, environmentally friendly and low-odor. This was the high standard they aspired to when the system partners began the actual test phase for their future project the following year.

Functional Coatings from the Plasma Nozzle

The creation of a boundary layer between two dissimilar materials presents the developers with a major challenge, since the chemical properties of the layer call for the creation of a simultaneous bond between different materials. The task becomes even more complex if the materials belong to different groups, as is the case here with metal and plastic.

Arthur Grishin, Project Leader Industrial Coating Processes in the R&D department at Plasmatreat, who also developed the new layer, was responsible for the scientific supervision of the project. He summed up the project as follows: "Plasma-Plus 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 in combination with the adapted plastic compound it forms such a strong joint and tight seal that it takes on the function of an anticorrosive coating."

A precursor in the form of an organosilicon compound is added to the plasma to produce a coating. Due to high-energy excitation within the plasma, this compound is fragmented and deposited on the surface in the form of a vitreous layer. 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 level of corrosion protection. 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 (**Fig. 2**) enables it to be targeted with pinpoint accuracy to a precisely defined location, even at very high processing speeds. A 100 Nm thin coating, for instance, can be 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, Grishin and his team 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 »

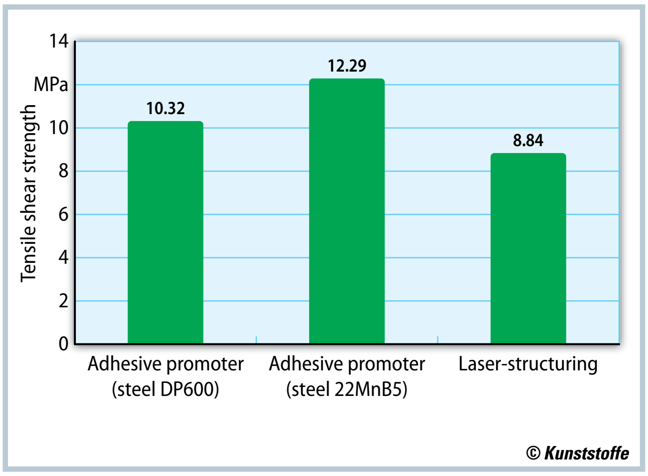

Fig. 6. Tensile shear strengths of steel coated with adhesion promoter and of laser-structured steel bonded to glass fiber-reinforced polyamide (source: ILK, TU Dresden)

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.

Adaptation of the Plastic Compounds

When formulating recipes for their plastics, manufacturers have to take into account many characteristics of the subsequent product stipulated by the customer – mechanical, electrical, thermal and chemical properties, the plastic's fire rating and its 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 components of the recipe 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. Akro-Plastic, which specializes in complex, customized adaptations of plastic properties and has developed its own compounding technology which enables the above-mentioned requirements for functional integrity and quality to be met internationally regardless of the production location, took on the task of creating a plastic compound with specific properties for the project. "The chemical recipe had to take account of two main aspects", said Düvel, "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."

Bond Strength in the Test Phase

For the test phase Düvel and Enneking focused on a glass fiber-reinforced type PA6GF30 plastic for the base compound, which was modified as testing progressed. Aluminum, steel, stainless steel and copper were used as the metal substrates to which the plastic was to bond. The two project managers and their teams tested around 1,500 test specimens of the different metals and modified plastic compounds, during which time Plasmatreat continuously optimized the PlasmaPlus layer in terms of both adhesion and protection against corrosive media. Right from the start, mixed fracture tests showed that fragments of the glass fiber contained in the plastic were firmly anchored in the plasma polymer layer (**Fig. 3**). After further modifications, the desired cohesive fracture of the plastic was finally obtained with steel, stainless steel and copper (**Fig. 4**). A mixed fracture was obtained with aluminum and galvanized steel. Tensile shear strength values in excess of 20 MPa and tensile strengths of over 80 MPa were obtained for the metals with cohesive fracture, with the best performing stainless steel bond even surpassing 27 MPa and 85 MPa respectively (**Fig. 5**).

By way of comparison, the Institute of Lightweight Engineering and Polymer Technology (ILK) at the TU Dresden, Germany, also conducted tensile shear strength tests using PA6GF30, but with different surface treatments. Here, the maximum tensile shear strengths obtained from steel – coated with a thermoset adhesive film and from laser-structured

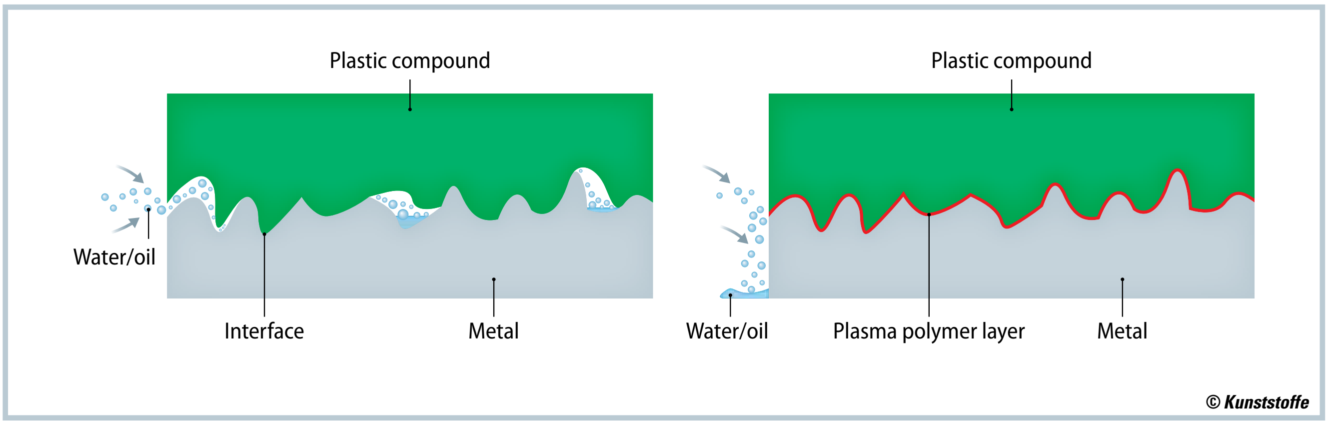

Fig. 7. The PlasmaPlus effect: Water penetrating the boundary layer of the plastic-to-metal bond can lead to corrosion, failure of the component function or even delamination (left). The plasma polymer layer (right) however prevents this by filling every available cavity, leaving the water no opportunity to penetrate the boundary layer; the chemical bond acts as a corrosion-proof barrier (source: Plasmatreat)

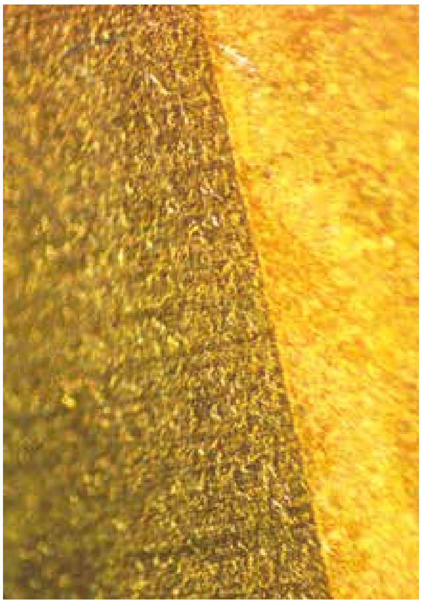

Fig. 8. Clear distinction: The micrograph shows the plasma-coated, corrosion-free metal surface (left) and the uncoated, corroded area (40 x magnification) (© Plasmatreat)

steel, both of which were bonded to glass fiber-reinforced polyamide, are well below the maximum values obtained with PlasmaPlus (**Fig. 6**).

Media Tightness as Corrosion Protection

Water can easily penetrate the boundary layer (**Fig. 7**) and spread across the surface of materials that do not have a chemically bonded connection. With the hybrid component described here, water in combination with oxygen would lead to corrosion of the metal, failure of the component function or even delamination. The PlasmaPlus layer prevents this effect by filling in microscopic cavities like a fine mist, bonding to the metal surface and forming a corrosion-proof barrier.

Tests carried out to date on the media tightness and corrosion resistance of plasma-coated metals have shown that the layer forms a barrier against water, salt solutions and gases and thus prevents the migration of these media. A test specimen demonstrates these findings: One half of a metal test specimen was coated with PlasmaPlus. Both halves were overmolded with plastic and then placed in a corrosive medium for several weeks. On removal, the plastic was mechanically removed and the metal was tested. There was a sharp distinction between the uncoated, now badly corroded area and the plasma-coated, corrosion-free metal surface (**Fig. 8**). Investigations of oil and other media tightness are currently under way, with preliminary tests already showing very promising results.

Summary

This innovative coating process offers a pioneering solution for improving plastic-to-metal bonds in the injection molding industry. The system partnership between the two specialists provides users with a particularly high degree of security for customized requirements. The new process also ensures greater product quality and a reliable, reproducible and cost-effective production process, whilst at the same time being completely environmentally benign. ■