Almost Inseparable

Strong Adhesion in Metal-Polymer Compounds due to Nanoporous Adhesive Layer

Although the use of different materials is one of the prerequisites for light and high-performance parts, the interface between metals and polymers is often the weak point of hybrid components. Now, however, nanoporous adhesive layers can be used to create permanent, reliable and practical joints.

The direct application of a polymer onto a metal component, without the use of additional adhesives and a resource-intensive pretreatment of the surface, is desirable from a technical, economic and ecological perspective. The Fraunhofer Institute for Chemical Technology (ICT) in Pfinztal, Germany, has developed such a process. Plasma-enhanced chemical vapor deposition (PECVD) is used to deposit a thin porous adhesive layer onto a metal surface, in a quick and simple process step. The adhesion of the nanoporous layer results from the infiltration of liquid polymers into the pores. Where the polymer solidifies through cooling or cross-linking with the pores, the interlocking effect leads to very high levels of adhesion. An investigation of the interface strength of PPS metal hybrids shows that the adhesion can be improved by up to 400% by using nanoporous coatings rather than mechanical methods, and by approximately 200% compared to chemical pretreatment.

Adhesion is achieved through the mechanical interlocking of the polymer with the pores in the layer. For this reason, in contrast to chemical activation methods, the nanoporous layer does not lose its adhesive strength over time, i.e. the layers can be stored for many weeks without any difficulty.

Furthermore, this process is an economically viable alternative to established pretreatment processes. Advantages include the short process times of approx. 10s and the possibility to coat large surface areas instantly. Both factors compensate for the higher investment costs of the plasma unit. The inexpensive consumable materials silicone oil and oxygen further improve the overall cost effectiveness. In addition, the coated areas are not required to undergo post-processing.

How Does Plasma Technology Work?

Plasma consists of a gas or a gas mixture with a variety of neutral and charged particles in different excited states. The life span of the particles in the plasma depends on how often they collide with each other. This is the reason why low pressure conditions, which reduce the collision frequency, are preferred for many plasma processes. Low pressure also leads to highly reproducible conditions which are essential for the deposition of high-quality layers. If microwaves are used as an energy source, the plasmas produced have a very low ion and high electron energy. Such plasmas are cool and highly reactive, which allows a high coating rate of up to 20 µm/min without damaging the surface.

Plasma units consist of an evacuated container, the so-called recipient, a vacu-
um pump, and a gas inflow. The vacuum pump and the gas inflow are used to regulate the working pressure and the gas composition. The plasma is ignited and maintained by the microwaves. Because the microwaves are conducted coaxially, linear plasma sources can be constructed that are many meters long, ensuring a homogeneous plasma density over the entire length. If multiple sources are set up in parallel, planar sources can be established, which produce a homogeneous plasma (Title figure).

In the PECVD, complex molecules (precursors), which become gases via evaporation, and working gases, e.g. oxygen, are introduced into the plasma chamber. Because of the plasma, the molecules and gases react chemically, forming a layer on a substrate surface. By this means, chemically bound groups are formed, which can in turn bind and polymerize other chemically reactive molecules and gases. A variety of layers are possible. One example is the reaction between the precursor hexamethyldisiloxane (HMDSO) and oxygen:

$$(\text{CH}_3)_2\text{Si-O-Si(CH}_3)_2(g) + n\text{O}_2(g) + \text{plasma energy}\rightarrow x\text{SiO}_2(s) + y\text{H}_2\text{O}(g) + z\text{CO}_2(g)$$

The chemical equation shows that, due to the effect of the plasma, the precursor HMDSO and the working gas oxygen react, causing a transparent glass layer to form on the substrate surface. If only the precursor HDMSO is exposed to a plasma, the monomers produced polymerize onto the substrate and form a silicon-like layer. As a result of this flexible process design, layers with a variety of properties, e.g. hard/soft and hydrophilic/hydrophobic can be formed and combined to complex layer systems. Such layer systems are necessary to increase adhesion and compensate for the different properties of the metal substrate and glass layer, for example the thermal expansion coefficient.

**Nanoporous Adhesive Layer Generated in the Plasma Process**

By changing the plasma parameters (operating pressure, microwave output, gas flow, etc.) the glass-like layer can also be made porous. The porous layer structure forms independently of the substrate material and is very adhesive on metal, glass, ceramic and numerous polymer surfaces. Figure 1 shows a scanning electron microscope image (SEM) of the porous layer. The layer forms in the shape of columns, with only nanometers between them. The individual columns are porous. The coating process only takes a few seconds due to the quick formation of layers.

If a liquid polymer, such as a melted thermoplastic or a reactive resin mixture, is now applied to the surface, the liquid polymer will enter the pores and solidify, creating an interlocking effect. This interlocking of the polymer with the porous structure significantly increases adhesion in the joint. The adhesive strength of the nanoporous layer was tested with several substances, including polypropylene, polyamide, polyphenylene sulfide, polyurethane, epoxy resin and silicone. These polymers were also filled with glass fibers or carbon black. No influence of the filling materials was detected. The fillers do not seem to significantly inhibit the infiltration, as capillary forces lower the

![Fig. 1. SEM image of the fracture edge between the substrate and the nanoporous layer (© Fraunhofer ICT)](image-url)
viscosity of the polymer, compensating for the potentially inhibiting influence of the fillers.

A glass sample coated with this nanoporous adhesive layer and subsequently infiltrated with liquid polypropylene shows a cohesive fracture behavior (Fig. 2).

Application for the Direct Connection of Metals to PPS

A study confirmed that the adhesive strengths of the nanoporous layer are significantly higher than those achieved using other methods of surface pretreatment. 3-mm aluminum, steel, and brass plates with a surface area of 100 x 100 mm² were produced. All metal surfaces were irradiated or coated with an adhesive layer. For the irradiation, 70-µm glass spheres were used, accelerated with an air pressure of 6 bar (~ 340 l/min). In addition, the plates were etched with phosphoric acid according to DTD915B (aluminum) or at 65 °C (steel). The residue that appeared on the steel surface was brushed off under clear water. Then the sample was dried in an oven at 120 °C for an hour. The brass surface was not etched, because etching is usually carried out with toxic sodium dichromate.

Polyphenylene sulfide plates were directly welded onto the samples without using any further adhesive. The tensile adhesive strength was subsequently determined according to DIN EN24624. Figure 3 shows the results of the tensile adhesive strength tests for the various surfaces and pre-treatments.

As shown in Figure 3, the nanoporous adhesive layers enable bonding strengths of approximately 22 MPa. This significantly exceeds the values of the other pretreatment processes. For instance, 12 MPa for etched aluminum and 10 MPa for steel were measured. Irradiation produces bonding strengths between 5 and 6 MPa. It is particularly interesting to note that these high bonding strengths are independent of the type of the metal. This suggests that the bonding strength is based on the mechanical interlocking of the polymer in the pores and not so much on the chemical interactions between the surfaces.

Conclusion

The results clearly show that the nanoporous adhesive layer is well suited for use in the manufacture of high-strength metal-polymer hybrid components. The layer does not lose its effect over time, and can be stored for weeks without any loss of quality.

The process of depositing a nanoporous adhesive layer does not include any toxic or dangerous substances, which means it is eco-compatible. Particularly short processing times and the possibility of coating very large surface areas justify the higher investment costs of the plasma unit. This process is therefore also economically attractive for mass production and for the manufacture of large components.