Metal and Polymer in Harmonic Bonding

Improvement of the Climate Change Stability of Electroplated Polymers

In addition to dimensional stability and quality of an electroplated layer system another important criterion is the adhesion between polymer and metal. This criterion places high demands on the material combination and the hybrid processing steps. Climate change tests according to automotive standards are used to validate it. To improve the quality of the hybrid material combination optimization processes have been developed.

In automotive applications the electroplating of polymers offers optimization potentials in weight and space utilization, free shaping by the injection molding process, and the refinement with a genuine metallic surface. Especially for decorative purpose and in the handle area electroplated ABS and PC/ABS parts are a quality feature of high-class automobiles. In contrast to very thin layer systems like PVD coatings (Physical Vapor Deposition) electroplated layers convince by genuine metallic haptic properties next to optical appearance and resistance against environmental influences. Electroplated metallic layers are emotional surfaces and increase also production efficiency through the combination of economical and physical advances of polymers, e.g., lightweight construction potential [1, 2].

Next to the requirements regarding surface brightness, scratch and media resistance, the bond strength of the polymer part and the metallic layer is an important criterion. Especially if mechanical stress is applied in the handling area, the adhesion between the different materials is safety relevant. Therefore, first stress simulations are done during the sampling, and climate change tests during series production. Process knowledge to optimize the interlinked production processes is compulsory to enhance the quality of parts with complex free shaped geometry. The German company BIA Kunststoff- und Galvanotechnik GmbH & Co. KG, Solingen, has examined different influencing factors on the hybrid material combination recently.

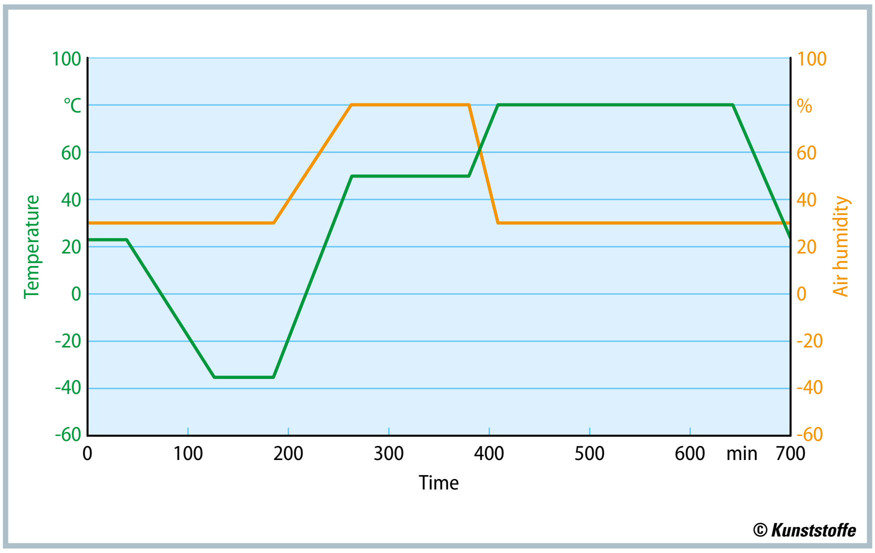

Fig. 1. Cycles with temperature and air humidity variation for climate change test PV2005 according to VW-specification TL528 [3] (source: BIA)

Climate Change Test to Validate the Bond Strength

So-called climate change tests apply cyclic load by varying temperature and air humidity (**Fig. 1**). The different coefficients of thermal expansion of the polymer (ABS: $9{,}5 \cdot 10^{-6}\,K^{-1}$) and the metallic layer (chrome: $4{,}9 \cdot 10^{-6}\,K^{-1}$) result in a mechanical tension at the boundary layer. The test simulates the stresses during usage, and the resulting potential failures by high temperature changes. Parts in the handle area have to endure 50 cycles of the test without any defects. So the risk of field failures can be minimized before the series production. Detailed knowledge on the influence criteria is necessary to optimize part geometry, material and production process in advance to be able to guarantee the high demands on parts even with increasing complexity.

Bonding Mechanism and Defects

The bonding mechanism of electroplated ABS-polymers is defined by a chemical pretreatment. The butadiene is oxidized by an etching process, afterwards the surface is activated via a palladium seeding. Within the boundary layer, the oxidizing forms caverns with small undercut geometries that enables together with the palladium the interdigitation of the »

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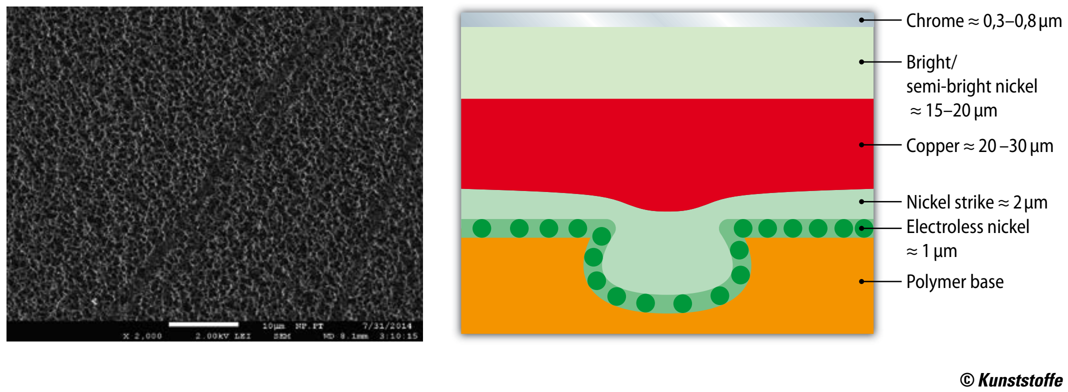

Fig. 2. Left: SEM picture of an etched ABS surface with visible matrix material and caverns; right: Layer system of electroplated parts according to automotive standards and interdigitation of the material combination (© BIA, source: BIA)

metallic layer in the leftover polymer matrix. Starting with the palladium, the closed layer system with copper, nickel and chrome is build up at the surface [4, 5].

Figure 2 left shows a SEM-image of an etched ABS surface. The oxidizing of the butadiene leads to the shown caverns with the remaining acrylnitril stylen as matrix material. The interdigitation of the layer system and its setup is schematized in **Figure 2 right**. A climate change test stresses the interdigitation within the boundary layer of the material combination and can lead to different defects. The cyclically applied stress can lead to two main failure categories:

- On the one hand an insufficient anchored layer will lead to blisters or cracks (**Fig. 3**). This depends on the etched surface and its caverns. If a too short etching time is applied or the polymer material is thermally damaged during the injection molding, the caverns are not developed properly. Due to high orientations and high shear rates applied by the injection molding process and the part geometry, the butadiene particles can be deformed or damaged by the dissipative energy. This interferes with the oxidative processes during the etching. If the matrix material is attacked by too high etching times, the properly developed caverns will be destroyed again which leads also to the mentioned defects as well.
- On the other hand the mechanical properties of the polymer raw material and the laminar setup of the component have an influence on the adhesion. The applied load during the climate change test is transferred via a good interdigitation into the polymer substrate through its boundary layers. If the polymer material is overstressed in the meantime, the layer system of the polymer part delaminates. An analysis of failure parts in this case remains of the polymer material on the backside of the detached metallic coating quite often.

The influences of polymer material, processing conditions during the injection molding and the electroplating parameters intertwine. Therefore, they have to be set up to the component requirements and material properties in each case.

Fig. 3. Delamination as possible failure and surface defect caused by climate change tests (© BIA)

Improvement of the Climate Change Stability

By an integral approach, electroplating parameters and processing conditions have to be taken into consideration. That is why etching time and reactivity of the etch are essential for the activation of the surface next to the accelerator and activator steps during the pretreatment. In this article the injection molding process and the material properties are focused. Stable conditions during the electroplating and the necessary layer thickness distribution have been secured.

Two different steps are possible to improve the climate change stability of electroplated polymer parts. On the one hand, optimization of the injection molding process can reduce the material load during the processing. On the other hand, a polymer material suitable for the requirements by part geometry, processing and application has to be selected. To be able to verify the influences of the processing parameters in injection molding, a test series with a part which has typical requirements and geometry for mechanical stressed parts in the handle area was done: a top cap for the gear level knob with dimensions of 20 x 35 x 10 mm (**Fig. 4**). The raw material is a standard ABS grade that can be electroplated. Injection velocity, mass temperature and mold temperature were varied during a statistic design of experiments (DoE) exemplary to validate the influences of shear, stress and thermal load (**Fig. 5**).

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Fig. 4. Exemplary gear level knop cap for the test series (© BIA)

The experimental results and the evaluation of the parts in two cycle steps show the influence of the processing parameters on the adhesion between the materials. Test points (y_i) that tend to build up orientations and internal stresses by low mass- and mold temperatures, show a high failure rate within the climate change test, e.g., y_1. This effect is amplified by high injection velocities (y_2). In combination, these results underline the influence of material stress and shear load during the injection molding processing for the adhesion.

The failure rate can be reduced by optimizations concerning internal stress via reduction of the material load during the processing. This includes a suitable mass temperature to secure a low viscosity as well as adapting the injection velocity and mold temperature to reduce the stress level during the filling. This implies the development of the failure rates of y_4, y_5 and y_6.

Beside the influences of the processing parameters, a specific behavior of all examples can be seen at 40 to 42 cycles. Even with optimized parameters, up to 60% of the parts failed within this test area. A detailed analysis of the failure parts showed that a good adhesion between the polymer substrate and the metallic layer system existed. Nevertheless particles of the polymer have been found at the backside of the metal coating, which implies that the boundary layer and therefore the polymer were overstressed.

Influence of the Base Material

Despite optimizations of the injection molding process, failures within the climate change test can occur related to overstress of the material. 50 components of ABS as well as PC/ABS materials with similar cap geometry were set up to show the potential of the selected materials. The parts have been tested with identical test conditions, of course the processing parameters have been optimized material specific to guarantee a minimized stress level and a steady filling of the mold.

The results of the second test series (**Fig. 6**) confirm the assumptions of the influences by processing parameters. The material ABS1 shows a nearly identical failure rate in this test series as it did in the one before. In addition, alternative ABS and PC/ABS blends can be processed with no failed parts up to 50 cycles. Nevertheless, the comparison of behavior of the different materials during the test series show that the failure rate between 32 and 44 cycles tends to increase because of an overstress of the boundary layer of the hybrid material combination. Materials with a low viscosity and a high heat deflection temperature (HDT(A) according to ISO75) comprise lower failure rates. The low viscosity enables a low injection velocity and thereby a reduction of the applied stresses.

A high heat deflection and a low coefficient of thermal expansion (**Table 1**) reduce the stress applied during the climate change test on the coating. Especially ABS2 with a high heat deflection and ABS/PC2 with a low viscosity and high Vicat softening temperature stand out. Both materials have a very positive behavior during the climate change test (**Fig. 6**). »

Material	HDT (A)	Vicat	MVR
ABS 1	92 °C	95 °C	24 g/10 min
ABS 2	98 °C	107 °C	6 g/10 min
PC/ABS 1	94 °C	110 °C	12 g/10 min
PC/ABS 2	94 °C	112 °C	26 g/10 min

Table 1. Comparison of different material properties like heat deflection temperature (HDT(A) and Vicat) and the melt volume-flow rate (MVR) for the tested plating grades (source: BIA)

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Company Profile

BIA Kunststoff- und Galvanotechnik GmbH & Co. KG, Solingen, Germany, supports the application-specific material selection already during the mold construction by process simulation with material behavior describing models. Subsequently the influence of the processing parameters is validated during the sampling to defy robust and steady processing conditions. This guarantees high quality surfaces, good adhesion of the coating and safe application even for critical parts.

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References & Digital Version

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	v_{inj}	T_{mold}	T_{mass}
y_1	–	–	–
y_2	+	–	–
y_3	+	+	–
y_4	–	+	–
y_5	+	+	+
y_6	–	+	+
y_7	–	–	+
y_8	+	–	+
y_9	Central point		

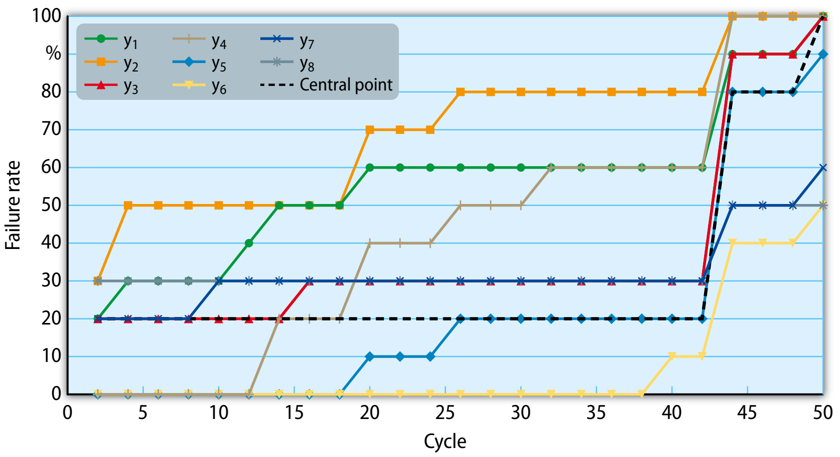

Fig. 5. Results of the climate change test: Around 42 cycles every test point y_i shows a high failure rate. Next to the injection velocity (v_{inj}) the mold temperature (T_{mold}) and mass temperature (T_{mass}) have been varied (source: BIA)

Conclusion

The results validate that the production of high quality surfaces using hybrid material combinations is influenced by several factors in polymer processing. The geometry of automotive interior parts requires a high level of processing knowledge. The application-specific polymer material selection and the process management of injection molding are the footing of a good adhesion between the layers. In addition, influences of the mold venting, charge variations and material condition of the polymer raw material, and the processing conditions during the electroplating cannot be ignored. So an integrated approach for process optimization is essential and a step by step optimization that also includes cost related influences is necessary. ■

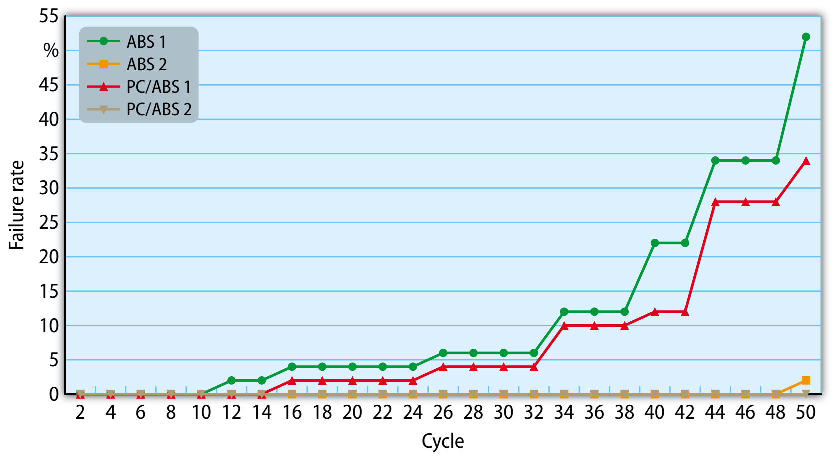

Fig. 6. The materials ABS 2 and PC/ABS 2 show a good behavior and resistance against the influences of the climate change test (source: BIA)

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