INFLUENCES OF PROCESSING PARAMETERS, MATERIAL, AND MOLD GEOMETRY ON THE SHAPE OF CAVERNS AS A QUALITY PARAMETER FOR ELECTROPLATING ON PLASTICS

Jens P. Siepmann, David Mazur, and Johannes Wortberg,
University of Duisburg-Essen, Institute of Product Engineering (ipe), Germany
Christian Notthoff, University of Duisburg-Essen, Nanoparticle Process Technology and CeNIDE
Felix A. Heinzler, BIA Kunststoff- und Galvanotechnik GmbH & Co KG, Solingen, Germany

Abstract

For automotive application processing technical polymers like acrylonitrile butadiene styrene (ABS) or polycarbonate blends (PC/ABS) with injection molding and refining them by electroplating is state of the art. The surface quality and processing parameters during the injection molding mandatorily influence the resulting part quality. Besides the electroplating parameters, the surface of the injection molded part is responsible for the conjunction of the polymer and the metal layer system. The surface and adhesion of the hybrid material combination is defined by etching butadiene in the part surface to a cavern structure.

An objective evaluation method for quantifying the two-dimensional shape of caverns is developed by using image analysis. The analysis is based on scanning electron microscope (SEM) images of chemical etched polymer part surfaces (ABS, PC/ABS). For quantifying the surface, meaningful key figures (e.g. roundness, degree of orientation, caverns/\(\mu m^2\), and area of caverns) are emerged. Finally, different materials, etching times, and processing parameters are compared to results of climate change tests and the analytical valuation of the surface structure.

Introduction

Due to the lightweight construction and the realization of complex geometries in an economical and resource-saving production process, the use of plastics in the automotive industry has become indispensable. Visual and tactile properties are realized by surface-finishing processes. One of these methods is the electroplating of injection molded plastic components. This process allows to make use of the weight advantages of plastic parts, while offering the high quality impression of a metallic component [1].

To comply with the stringent quality requirements of the automotive industry on electroplated plastic components, a linked-up manufacturing process with integration of all entities is necessary [2]. Hence, for the electroplating process seven entities influencing the electroplating processing chain (customer, construction, mold construction, injection molder, material manufacturer, electroplater, merchant) should be incorporated [3]. Therefore, the quality of the final product depends on the accuracy of the whole process. Considering the manufacturing of parts with corresponding attributes of functionality, geometry, visual and haptic effects, and quality, key processes are the injection molding and mold construction. In general, deviations of the quality requirements cannot be detected before the electroplating process is completed. Reject in production leads to expensive recycling processes because of the required additional separation of the polymer and metal layer. Hence, it is crucial to detect failures before the electroplating process takes place. To achieve this goal, knowledge about the influence and interaction of the injection molding process with the shape of the caverns at the part surface, which are basis for adhesion, is required. To date, no direct method of analyzing the part quality and correlating the part surface properties with the processing conditions and adhesion of the layer system exists. In this paper, the basic analysis of influences on the shape of caverns as well as their quantification using an image evaluation algorithm, is presented.

State of Orientation at the Edge Layer

During the filling phase of the mold, the macromolecules of the polymer melt get aligned towards the occurring shear and strain stresses. While there are different velocities perpendicular to the flow direction at the shear, the strain is based on velocity differences in flow direction [4].

As the melt gets in contact with the mold, the infinitesimal-sized emerging edge layer adapts the temperature of the cavity wall and forms a highly oriented edge layer, without the possibility of relaxation. Hence, a biaxial state of orientation with more marked longitudinal orientation occurs. Concerning the cross section of the part, the highest orientation can be found at the surface [4],[5]. The more the injection velocity increases, the stronger the state of orientation in the emerging edge layer increases, while the orientations inside the part decrease. This can be ascribed to higher shear loads, the rise of melt temperature, and the isolation of the melt to the cavity wall caused by low heat conductivity of the edge layer and a higher relaxation time inside the part [4].
Characteristics of Surface Formation

The phenomena illustrated for monophasic polymers do also exist for polymer blends. Because of the multiphasic system (e.g., PC/ABS-blend) additional influences on the formation of the morphology inside the part and at the surface occur. These are the mixing ratio, the viscosity ratio, the elasticity of the components, the interfacial tension, and the original morphology [6]. As viscosity ratio affects the phase segregation, deformation, and coagulation [7],[8], it is highly important for the surface formation. For a low content of ABS that means that a bead-and-string structure occurs. On its way to the flow front, the rubber-modified polymer is in spherical condition, while there is a stretching of the ABS at the cavity wall [7]. For an markedly higher amount of ABS, PC can be found as dispersion stretched at the cavity wall.

In addition to that, another phenomenon can be detected with PC/ABS blends. The part is covered by a very thin PC layer, which can be explained by the materials’ flow properties. Because of the lower molecular weight of the PC, the flowability of the PC is better than the flowability of the ABS. Therefore, the PC covers the flow front and is deposited at the cavity wall while filling phase. High loads of the melt can cause crack initiation because of instabilities of the fountain flow and a thermal degradation of the butadiene. By that phenomenon, the ABS phase reaches the cavity wall and solidifies [9],[10].

Processing Parameters and Mold Geometry as Influences to Part Surfaces Respective Electroplating

Basically, the increase of frozen-in stresses inside the part leads to a decrease of the peel strength [2]. Additionally, stresses at the part surface cause the straining of the butadiene particles during the processing [11]. Stress relaxation and unfavorable cavern structures may result in peeling effects and blistering. The state of stress is not only influenced by the filling phase and the orientation, but also by injection molding parameters like the cooling rate, affected by the mold temperature, the melt temperature, and the injection velocity [2],[12]. The main cause of morphology change for polymer blends is the extensional flow with different morphology inside the part and at the surface [11]. For a good adhesion without defects in the metallic layer, a uniform distribution of the butadiene particles in the near surface area is achieved [13],[14].

For the production of electroplated polymer parts, not only directives for injection molding suitable part design must be considered, but also electroplating directives should be taken into account. The main goal in mold design for electroplating is the same as for processing parameters, namely the state of stress and orientation of the part. Areas with higher stresses are more affected by the chrome sulfuric pickle (aqueous solution containing chromium trioxide, sulfuric acid and trivalent chromium with a perflourinated wetting agent at 60-70 °C) and thus local over- or underpickling may occur. These stress differences can be minimized by optimizing the part design regarding different wall thickness and reduction of the cross section [12]. Specific construction directives or guidelines can be found in [2],[3],[12],[13],[15].

Image Analysis Algorithm and Experimental Setup

In general science, image analysis as a process, as depicted in figure 1, is a common tool to enable quantitative and objective investigations of images. Furthermore, findings can be achieved which are not possible with other metrology [16].

![Figure 1. General procedure of image analysis](image)

The developed algorithm is shown in figure 2. The original SEM image of the part surface, captured with the lower secondary electron image mode (LEI) with a JEOL JSM-7500F, is edited by employing contrast optimization, binarization, a noise filter, segmentation, and the ellipse fitting using ImageJ.

![Figure 2. Procedure of the image analysis algorithm](image)
The ellipse fitting results are shown exemplarily in figure 3 in comparison to the original structure, which can also be seen on the image. The fitting result data is evaluated regarding the orientation angle $\alpha$ of the ellipse major axis and $x$ axis orthogonal to flow direction ($y$ axis), the roundness as the ratio of major and minor axis with a value of 1 for ideal roundness, the cavern area, and the number of caverns per $\mu$m².

![Figure 3. Ellipse fitting results compared to original image and illustration of the meaning of the orientation angle](image)

**Experiment and Validation**

For the validation of the image analysis algorithm, tests are conducted to investigate whether differences in the key figures mentioned above can be detected. Therefore, SEM images of two part surfaces (figure 4) were captured at the marked spots. The standard-2-plate part consisted of an ABS (Novodur P2MC) and the automotive button consisted either of an ABS (Novodur P2MC) or a PC/ABS-blend (Bayblend T45 PG) in order to compare material dependent differences.

![Figure 4. Preliminary test standard 2-plate-part (a) and automotive button (b) with SEM image capture spots](image)

For the standard 2-plate part one measuring point was defined and the screw advance speed was exemplarily set to 10, 40, and 80 mm/s. For the automotive button part, two points are investigated with different etching times of 8, 12, and 16 min.

The orientation angle results for the 2-plate part are shown in figure 5. The subjective impression of a distortion of the caverns in flow direction depending on increasing screw advance speed on the SEM images can be analyzed and now quantified by comparing the increasing standard deviations (SD) indicating a higher distortion of the orientation angle. In addition to the changed parameter, a comparison of the magnification is also depicted in figure 5. The higher optical magnification shows just a small excerpt of the surface area captured with the smaller magnification. Therefore, the weighted average (WAVG) angle differs from 0.8 to 4.1%. In combination with the SD, the increasing distortion of the two-dimensional shape of the caverns can be detected with both magnifications. For the roundness, a WAVG value between 0.69 and 0.71 is measured independent of the velocity.

![Figure 5. Orientation angle results (90° flow direction) for produced standard 2-plate-parts with 10 (a), 40 (b), and 80 mm/s injection velocity, magnification of 5,000x (5K) and 10,000x (10K)](image)
For the key figure caverns/µm², the results for the automotive button dependent on the position on the part and etching time are presented in figure 6. For the ABS, the number of caverns is nearly constant from 7.27 to 7.83 1/µm² at the center, while the number increases from 6.66 to 8.75 1/µm² at the edge. Different results can be found for the PC/ABS. While the number of caverns increases from 5.26 to 7.56 1/µm² at the center, at the edge a number of 9.05 1/µm² is already reached after 8 min. This discrepancy can be referred to the area of the caverns, which is rather small for PC/ABS at the edge (50,000 nm²) compared to the ABS (65,000 nm²).

For the ABS at the part edge, the results may be explained by the higher shear rate. The high shear rate region at the edge causes a higher impact of the chrome sulfuric pickle so that the number of caverns increases faster by increasing etching time than for the ABS center position. A possible reason for the lower number of caverns at 8 min etching time (edge) is the higher load by shear rate and shear heating causing a higher resistance to the pickle impact. For the PC/ABS center at 8 min etching time a lower number of caverns is measured compared to the ABS. That can be explained by the thin PC layer covering the part. At the edge a different result can be detected. First there is a slight increase of the number from 8 to 12 min and then a decrease to 16 min. That indicates a unification of the caverns.

Quality Criteria

The presented investigation shows a correlation between the processing conditions and the analytic results. To correlate these insights with actual quality criteria such as adhesion of the material combination in a climate change test, a final evaluation is done. Therefore, an automotive part is processed with different polymer materials with stress reduced optimized injection molding properties. To demonstrate the material influence and to vary the cavern structure, the etching time within the electroplating was extended from 8 and 12 to 16 min. Depending on the material’s reaction to the oxidative etching process this leads either to insufficient cavern structures on the surface or a reduction of the matrix material and therefore destruction of the cavern structure at high etching times.

To control the quality of the material combination, a climate change test (CCT) according to DBL8465 [17] is applied to the parts. Figure 7 shows the failure rate of different materials according to the etching time.

On the one hand, if the cavern structure is not formed well by a reduced oxidative etching process, blisters occur during the test. This reaction is comparable to the processing influence of high shear rates and the thermal destruction of the butadiene. On the other hand, high etching times can cause a reduction of the undercut structures as well as a destruction of the acrylonitrile styrene matrix and thus lead to an insufficient etching structure. As the etching time is material specific, the remaining matrix material cannot accommodate the stresses during the CCT and therefore a delamination of the layer system occurs.

For ABS1 (Novodur P2MC White), a better activation of the surface and adhesion of the material layer combination can be achieved by increasing the etching time. This indicates a better shaping of the cavern structure. The analysis by the described algorithm shows a better distribution and reduced orientation of the caverns by increasing the etching time. In addition, a significant enlargement of the cavern area from 8 to 12 min can be detected (figure 8).
It can be concluded, that for ABS2 (Novodur P2MC HH), 8 min etching time are insufficient, whereas 16 min are too high. At these setups very high failure rates occur. This correlates with the cavern areas on the surface detected by SEM and calculated by the presented algorithm. The WAVG cavern area increases from 8 to 12 min, but decreases mandatorily from 12 to 16 min (figure 9). This is supported by the results of the CCT. On the one hand, an insufficient etched surface leads to a delamination of the material layers. The electroplating material cannot be embedded within the surface layer of the polymer part and the low amount of cavern structures. On the other hand, a high etching results in a destruction of the matrix material and cavern structure. The stresses during the CCT break the matrix structures and thus delamination as blisters occur again.

![Figure 9. Analysis of the SEM image for ABS2](image)

For the considered materials, a correlation between the analysis of the SEM images and the results for the layer adhesion can be derived. The subjective impression (figure 10) of the etched surface can not only be verified by the calculated values, but also be explained by the different results in the CCT.

![Figure 10. SEM images for ABS1 (a) and ABS2 (b) depending on etching time](image)

**Conclusions**

The investigation shows that the developed image analysis algorithm for quantifying the two-dimensional shape of caverns is an appropriate tool for analyzing the surface morphology of etched polymer parts before the plating process.

The chosen key figures can be used to describe the surface and relate the results of a climate change test to measurable properties of the caverns. The impact of processing parameters to the resulting key figures can be detected for different screw advance speed. Besides the material and its properties, the method of analysis shows geometry dependent variations of the key figures. It can also be concluded that the results are influenced by the SEM image quality and that high quality SEM images are hence important for deriving significant results.

Further work will deal with investigations concentrating on processing parameter variations in injection molding for different materials and different spots on the part surface considering shear loads. SEM images of etched part surfaces are evaluated with the image analysis algorithm.

**References**