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Molded parts with functional surfaces – how laser microstructuring can be used for low-cost mass products

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Abstract

Microstructuring via ultrashort pulse laser enables the targeted generation of functional surface structures. With this technology, progress in material behavior has been shown in tribological, optical and haptical properties, liquid wettability and cell adhesion. In cases where the effect is mainly based on the laser-generated microstructures instead of laser-induced chemical changes of the surface material, injection molding offers a possibility to make the usually high-priced laser surface functionalization accessible to low-cost mass products. This technique leaves the chemistry of the molded parts unaffected, which makes it especially attractive for biomedical applications. Molding inverts the surface topography and can be associated with resolution, durability and demoldability restrictions. We present our current results and findings on basic as well as on application-oriented issues. Selected applications including a technique for piracy protection are discussed.

Keywords: microstructuring; surface functionalization; molding; ultrashort pulse laser

1. Introduction

The microstructuring and surface functionalization of components using ultrashort pulse lasers enables the creation of innovative and functionally optimized products. However, the creation of laser-generated functional surfaces is associated with expensive equipment and high production costs. In order for the advantages of this technology to reach the mass market, it is advisable to combine it with processes designed

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for mass production. Laser processing can generate a variety of surface structures on injection molds that would not be possible with other machining techniques. These structures can then be transferred to injection molded parts and provide new functionalities on the surfaces of these parts. Directly laser-machined polymers can exhibit chemical changes due to photo-oxidation as described by Assaf and Kietzig, 2018 and chemical bond breaking as described by Chatani 2014, which is not always a desirable side effect of surface functionalization. This may even be a criterion for exclusion, especially in the case of medical products. However, if only the injection mold is structured, the structures can be transferred without any chemical change on the injection-molded parts.

When creating such surface structures in molds and molding these structures, there are several problems to address. With stochastic surface structures such as ripples or spikes as shown by Reif, 2018 the surface is first scanned with the laser. Laser process parameters such as pulse energy, pulse spacing and repetition rate determine surface topography features such as average structure distances or aspect ratio. This topography then ensures a functional interaction with, for example, light or water. While the targeted material removal is already understood, the targeted function generation via an adjustment of the laser parameters is not yet sufficiently understood. Scientists and process engineers can only estimate this with the help of empirical values or document it through elaborate laboratory tests. If the molded structures are to have the desired property, the negative of the functional surface topography has to be generated on the mold. In the case of structuring injection molds, there is also the fact that the functional surface should exist on a polymer, whereby the injection mold is made of metal. However, it is difficult to generate and test the functionality of the structures directly on the polymer parts in advance by means of a laser ablation, as there is a chemical change in the material that could have an influence on the functionality. However, Groenendijk, 2008 shows that molding of a hydrophobic structure can also lead to a hydrophobic structure on the molded part.
If you want to have a desired functional surface on an injection molded part, the following steps are necessary:

- Identify a surface topography on the injection molded part that will provide the desired function.
- Invert the topography for the mold
- Find a parameter set that can be used to create the inverted topography.

Besides the generation of stochastic surface structures, the implementation of deterministic microstructures such as trenches or wells is also interesting. Here the procedure is easier, as only the inversion of the topography and the molding behavior from the injection mold have to be taken into account. This paper presents recent work on the creation and molding of laser-generated deterministic and stochastic structures.

2. Experimental Setup

The following tests were carried out on polished specimens made of the plastic mold steel 1.2083 with a thickness of 10mm. Replisil 22NF was used to mold the structures produced. The laser source used is a diode-pumped ultra-short pulse laser (Coherent Monaco) with a wavelength of 1035 nm, a pulse duration of 252 fs, a maximum pulse energy of 80 µJ and a maximum repetition rate of 50 MHz. The optical setup consists of a beam expander and a 100 mm focal length F-theta lens. The samples were positioned on an x-y translation stage. The samples were analyzed with a laser scanning confocal microscope (Keyence VK-X1000).

The aim of the first study is to create homogeneous, raised honeycomb structures on the injection-molded components for cell biology applications. Accordingly, trenches with a uniform depth and width are to be created into the injection mold by laser machining. The honeycomb structures should have a diameter of 250 µm and a height of 50 µm. When creating trenches in the injection mold using ultrashort laser pulses, many parameters must be taken into account in order to achieve a satisfactory result. The material removal per pass decreases the deeper the material is removed. In order to determine a process window with which a targeted cutting depth can be achieved, ablation tests are first carried out. The same structure is applied to the workpiece several times in succession and then evaluated by means of microscopy. The parameters used are shown in Tab.1.

Table 1. Processing parameters

Processing parameters	Value
Iterations	50
Line spacing	5 µm
Fluence	0.4-4 J/cm²
Focus diameter (@1/e²)	26 µm
Scan speed	500 mm/s
Repetition rate	200 kHz

3. Results

The data set created (fig.1) shows the average ablation depth achieved per pass for 50 repetitions with the respective fluence. When looking at this ablation curve, it becomes clear that in the range between 0.4 J/cm² and 0.9 J/cm², even small changes in fluence lead to a strong change in the ablation depth per pass. Between 1 J/cm² and 3 J/cm² there is an ablation regime in which the ablation depth per pass is not so much affected by fluctuations in pulse energy. In this regime, the best machining quality was also observed. Heat-affected zones were not present and the trenches run evenly and with low surface roughness. From a fluence of > 3 J/cm², the removal depth per pass increases somewhat more. The accuracy of the process decreases and heat-affected zones could be observed at the trenches. Based on these results, a fluence of 1 J/cm² was selected for the machining of 1.2083, since a low removal depth per pass is still guaranteed here and the process can thus be finely adjusted. At the same time, the removal per pass is not as susceptible to process-related deviations in the fluence as is the case below 1 J/cm².

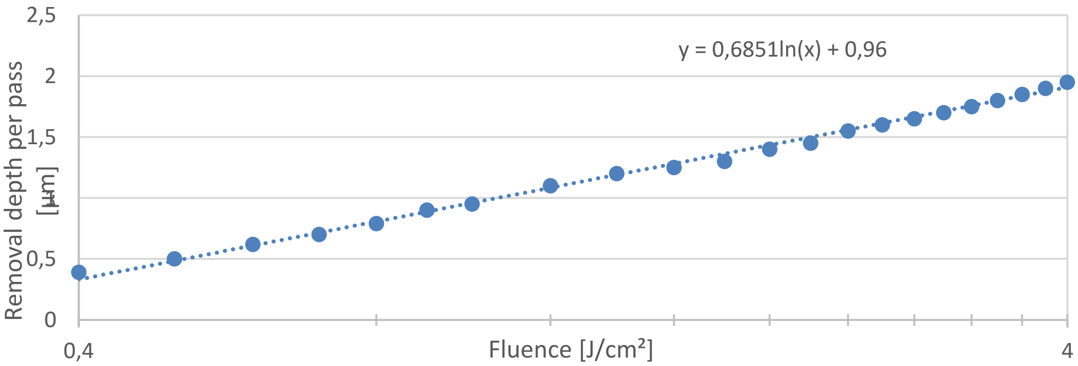

Fig. 1. Depth of removal as a function of laser fluence

It is also crucial for the machining quality that no spot is hit more than once per pass, otherwise there will be large differences in the removal depth. The scanner delays have been optimized for this. The scanning speed must also be kept constant. The scanner should therefore be at speed before the laser is switched on and only slow down after the laser is switched off. After creating the trenches on the injection mold, it was cleaned with compressed air. Afterwards, the created structures were molded with Replisil 22NF. The molded honeycomb structures can be seen in Fig. 2a and 2b. The height of the created structures is 50 µm, with slight deviations in the single-digit µm range. At the corner points, where 3 walls meet, no significant deviation of the wall height and thickness can be seen. Characteristic for the laser ablation is the V-shaped profile of the

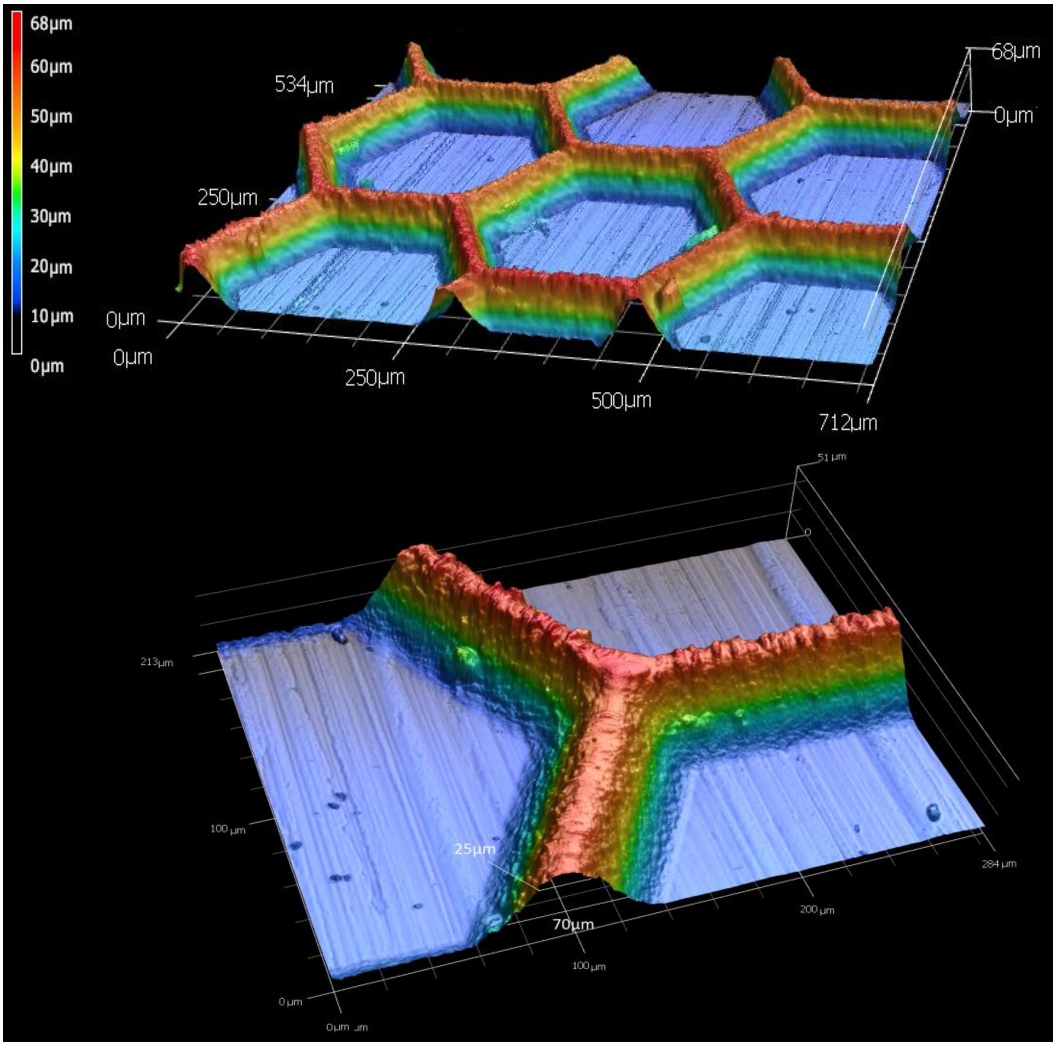

Fig. 2. (a) molded honeycomb structure; (b) close-up of an interface

wall. This favors the molding of the material, as no macroscopic undercuts occur. The wall thickness is approx. 70 µm at the base and approx. 25 µm at the apex. The walls have a significantly greater surface roughness than the polished underside. The reason for this is not only the ablation process but also the molding process. The laser ablation increases the surface roughness, resulting in microscopic undercuts on the walls. The impression material can tear off there during solidification and molding.

Besides deterministic structures, the transfer of hydrophobic surfaces is also investigated. The injection mold was equipped with different sets of hydrophobic structures as seen per example in fig. 3. Laser scanning microscopy cannot clarify whether nanostructures are present on the spikes. Here, only the microstructures are visible. The respective water contact angles were measured. The surface is then molded using Replisil22NF and the water contact angles are compared.

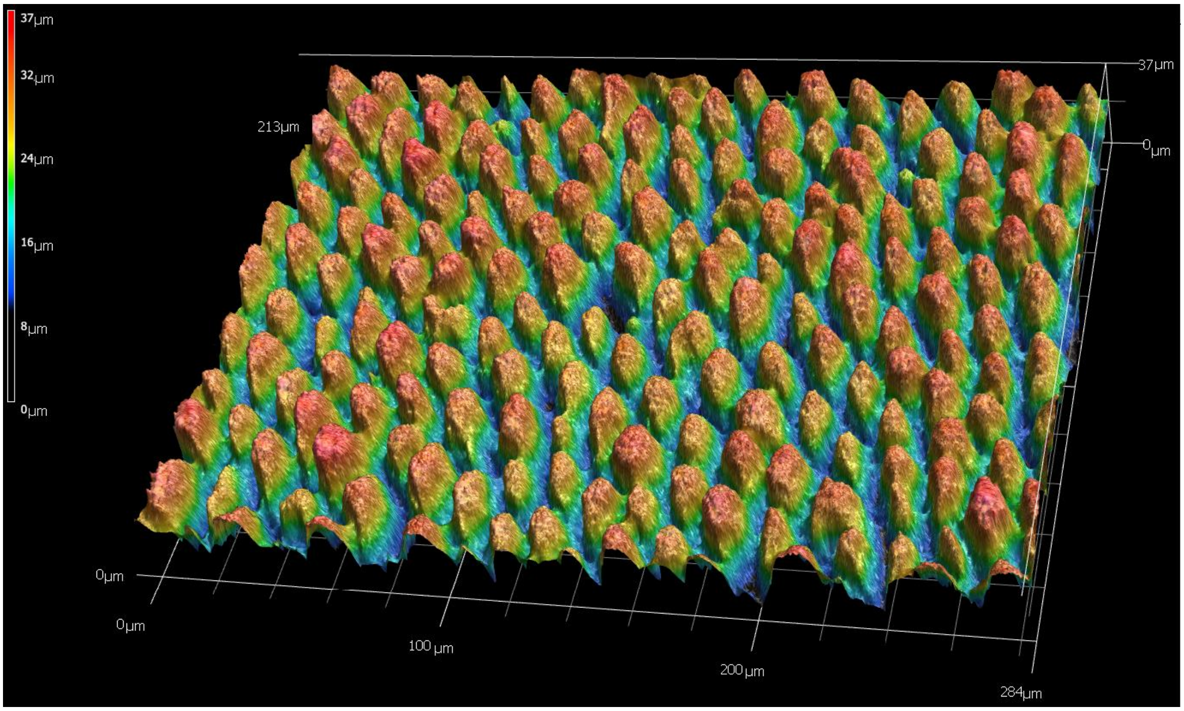

Fig. 3. Spike-formation on the injection-mold

Fig. 4 illustrates that the water contact angle between the molded part and the mold is similar. Thus, by molding a hydrophobic surface, a hydrophobic surface can also be produced. However, it can be observed that the greater the contact angle, the greater the difference between the two samples. There could be several reasons for this. The difference in material may have an influence on the contact angle. In addition, the microstructures may be damaged during the molding process. It is also possible that particularly small structures were not molded. This needs to be clarified in the further course of the project.

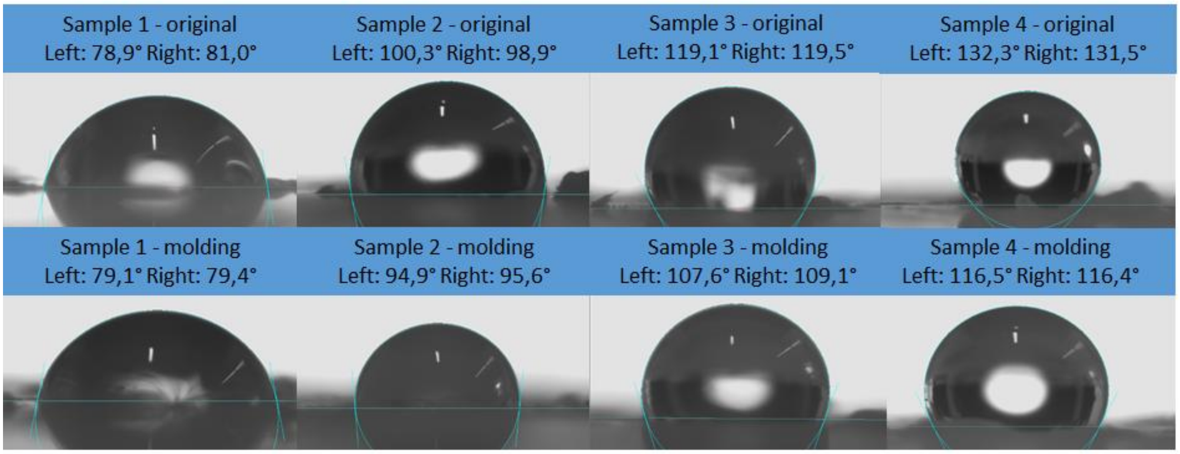

Fig. 4. Water contact angle on the injection mold and on the molding

4. Discussion

According to Wellershoff 1999, the ablation depth per laser pulse d_z is logarithmically dependent on the divisor of fluence (F) and threshold fluence (F_{th}) according to formula (1), whereas d_0 describes the effective penetration depth.

$$d_z = d_0 \ln \frac{F}{F_{th}} \quad (1)$$

This logarithmic relationship could be confirmed in Fig. 1. However, the formula (1) only apply to single laser pulses. As soon as several pulses overlap and many iterations are performed, it is no longer possible to precisely predict an ablation depth. Heat influence and the change in surface roughness falsify the expected results. Therefore, it makes sense to evaluate desired ablation depths in laboratory tests in advance.

Laser structuring of injection molds offers the possibility of generating functional surfaces on inexpensive injection molded parts. Since the laser does not come into direct contact with the polymer and no further processing steps of the injection molded parts are required for surface functionalization, this technology can efficiently increase the value of the injection-molded parts. Initial tests show that both deterministic and stochastic structures can be molded with satisfactory quality. Deterministic structures can be created and molded with an accuracy down to the single-digit micrometer range in all three axis directions. However, a considerable change in surface roughness must be expected due to laser structuring. Possible undercuts can impair the molding process. When creating deterministic surface structures, typical laser ablation characteristics such as the V-shaped depth ablation profile must therefore be considered.

Due to their properties, stochastic surface structures offer yet another interesting application. Due to the random structure arrangement, it is almost impossible to copy them. If these micro and nano structures can then be applied to the injection-molded parts by means of injection molding, the parts can be clearly assigned to the injection mold used. If corresponding images of the injection mold are taken, like in fig. 3, plagiarized parts can be distinguished from original parts. Although it has already been shown that hydrophobic surface features can be molded to a certain degree, the extent to which ripples or spikes can be molded in the submicrometer range still needs to be investigated in more detail. The molding process will play an essential role in this. Subsequent molding tests should be carried out using high-resolution processes such as variothermal injection molding. In addition, scanning electron microscopy must be carried out to investigate possible nanostructures.

5. Conclusion

In this paper, the generation of deterministic and stochastic surface structures in injection molds using a femtosecond laser for medical technology was investigated. Since the injection molded parts themselves do not come into contact with the laser radiation, a chemical change of the molding material due to laser radiation can be excluded. The structures produced were molded with Replisil and examined. Through a previously conducted parameter study, the honeycomb structures could be created with an accuracy down to the 1-digit micrometer range. The impression corresponds to the previously set specifications for diameter and wall height. The measurements of water contact angles of the hydrophobic surface structures show that hydrophobic structures can be transferred. The functionality does not require further topography inversion. However, with increasing water contact angle, the original and the mold differ increasingly from each other. It is suspected that nanostructures were either not molded or that they were destroyed during the molding process. Unfortunately, the laser scanning microscope cannot detect these structures. Further tests with variothermal injection molding are planned. In addition, SEM investigations should provide further insights into the existence and molding of nanostructures.

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