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Lithography-Based Ceramic Manufacturing (LCM) for Dental Applications

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Abstract. Dental applications like crowns, veneers or bridges require high accuracy to be fitted on the patient's stump. Stereolithography is an additive manufacturing method, which offers high precision by using light exposure as the layer generating mechanism. In the LCM process, this precision is combined with a thermal post-processing step to achieve full ceramic restorations. The overall production of such ceramic parts in a reproducible way is a highly complex procedure.

The first requirement is to find a slurry formulation, which is stable against sedimentation and segregation, that is also processable in a stereolithographic system. Such a formulation has been found by us, which could be shown by rheology measurements. During experiments with this formulation, it could be observed that there is a correlation between wet film thickness and resolution. Several adjustments to the machine have been made, to fully control this parameter. Namely, changes to the vat, the doctor blade and the building platform have been made. The improvement of the process and the quality of the final parts are validated by fabricating Siemens stars and by biaxial bending tests.

Introduction

The manufacture of full ceramic bodies is an essential tool in the field of dental restorations. It is state of the art to produce those parts via CNC-mills (computerized numerical control). [1] In contradiction to the subtractive process, another possibility is to use additive manufacturing (AM). One of those AM technologies is stereolithography, which uses light to induce photopolymerisation. This AM technology offers the advantage of producing several restorations at the same time (limited only by the size of the building space), whereas CNC-mills are limited to producing one restoration consecutively. The light source for stereolithography can be either laser or digital light processing (DLP).

The machines at TU Wien use DLP to perform the LCM process. In this process, photopolymerisation of an organic matrix is used to form a 3-dimensional object layer by layer. This matrix is filled with ceramic particles, which leads to the full ceramic part after burning off the polymeric matrix by thermal post-processing.

To ensure the reproducibility and quality of the manufactured parts there are certain requirements to the slurry system, i.e. the particles shall not sediment, the viscosity cannot be too high and the filler content should be high to enable quick binder burnout and a dense ceramic part. [2]

In [3] it was shown, that thixotropy additives can positively influence the rheological stability of the slurry while maintaining a shear-stress characteristic that is necessary for the coating mechanism used in this work. The inorganic additive however decreases the final mechanical properties due to not being burned out in the thermal post-processing step.

Therefore in this work, an organic dispersing agent was used, which maintains the thixotropy behavior and which is burned out during debinding.

Additionally, after maintaining a stable slurry formulation, a dependency of the wet film thickness on the resolution of printed parts could be observed. Following this observation several adjustments to the coating mechanism have been made, which are described in this text.

This text is meant to give the fundamental criteria, which enable the successful production of ceramic parts via AM, especially considering the rheology of the slurry, coating mechanisms and interaction between materials (coated glass plate) in contact with the slurry. To validate the material quality of the final parts, biaxial bending tests were performed.

Materials and Methods

Lithography-Based Ceramic Manufacturing. The machines at TU Wien are called 'Blue Printers', because they apply light in the visible wavelength range ($\lambda = 460$ nm) to initiate the photopolymerisation reaction. A schematic representation of those machines can be seen in Fig. 1.

The light exposure, generated by an LED, happens through the transparent vat from below. The exposed area is controlled via DLP by using a digital micromirror device (DMD) and the beam is widened by an optical lens system to the final pixel size of 40 µm.

The vat is circular and the coating happens via a doctor blade to enable a smooth, thin and evenly distributed film. Cured layers are taken off by a top-down building platform. To facilitate the take off, the vat can be tilted. Those steps happen in a repeating cycle to form a 3-dimensional object. Parameters like exposure time and intensity can be adjusted depending on the slurry formulation.

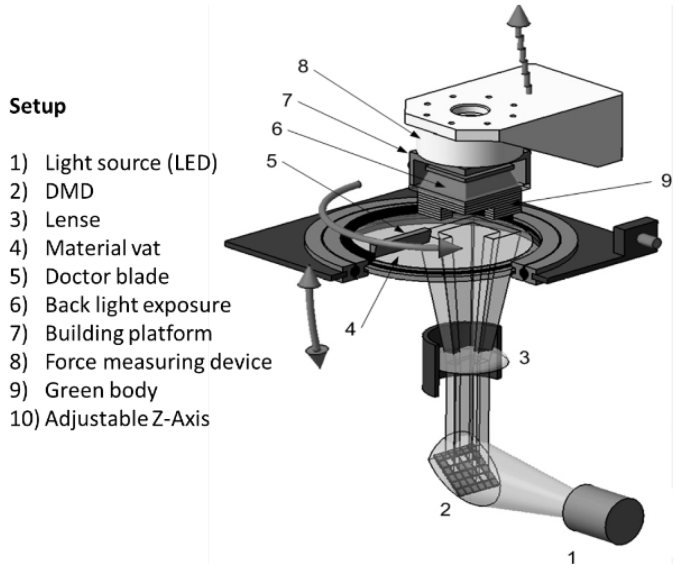

Figure 1. Schematic representation of the main machine elements of the *Blueprinter* 5.

Slurry. The formulation consists of a combination of two methacrylates, solvent, photoinitiator, a light absorber to reduce deviations of the desired polymerisation by internal scattering, a dispersing agent and the desired ceramic filler - in this case glass powder, which acts as a precursor for the subsequent generation of Lithium-Disilicate crystals to obtain the glass ceramic known in dentistry. The amounts of the components are listed in Table 1 respectively.

Rheometer. Rheological measurements were carried out using an oscillation rheometer "MCR-301" by Anton Paar GmbH, 8054 Graz, Austria and the associated software "Rheoplus", which was also used for interpretation. A cone-plate measuring system (CP25-1) with a gap width of 49 µm was used.

To characterize a slurry formulation, 3 measurements were carried out. A so called amplitude test, a frequency test and a step test. The amplitude test is carried out to find the area of linear viscoelastic behavior. A value inside of this area is taken for the frequency test. The frequency test gives information about the stability of the slurry and the step test allows to determine whether thixotropic behavior is immanent.

Wet Film Thickness. Measurements were carried out using a wet film thickness measuring device "Model 433" obtained from Erichsen GmbH & Co. KG, 58675 Hemer, Germany.

Table 1. Composition of a slurry for ceramic manufacturing.

Component	Amount [wt%]
Solvent	10 - 20
Monomer	10 - 20
Photoinitiator	< 0.5
Dispersing agent	< 5
Light Absorber	< 0.1
Ceramic Filler	60 - 80

Biaxial Bending Strength. Biaxial bending tests were performed according to the Norm DIN EN ISO 6872:2013 for ceramic materials in dentistry. A universal testing machine "Z050" of the company Zwick GmbH & Co. KG, 89079 Ulm, Germany, was used for this purpose.

Debinding. Debinding takes place in a ventilation oven "HRF 7/22" of the company Carbolite Gero GmbH & Co KG, 75242 Neuhausen, Germany, by temperatures up to 500°C.

Sintering. Sintering takes place in a vacuum oven 'Programat P700' for dental applications obtained from Ivoclar Vivadent AG, 9494 Schaan, Principality of Liechtenstein, at a maximum temperature of 850°C.

Results

Rheology. The area of linear viscoelastic behavior was determined previously reaching as far as a deformation of 0.04 %. The frequency test, shown in Fig. 2, was then carried out with a constant deformation of 0.01 % at 30 °C. The storage modulus (G') reaches higher values over the whole frequency range than the loss modulus (G"). This can be considered as a proof for slurry stability.

Fig. 3 shows the step test. Here 3 distinct phases are chosen. The first phase is a relaxation phase with a constant deformation of 0.01%. The second phase is the load phase. It begins after 1000 s. High shear stresses in combination with high frequency destroy the gel character and lead to the dominance of the viscous behavior. The gel character is automatically reestablished 1.05 s after the load phase has ended.

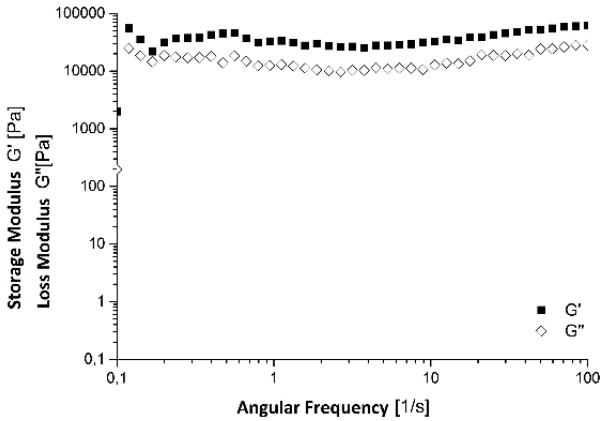

Figure 2. Frequency test.

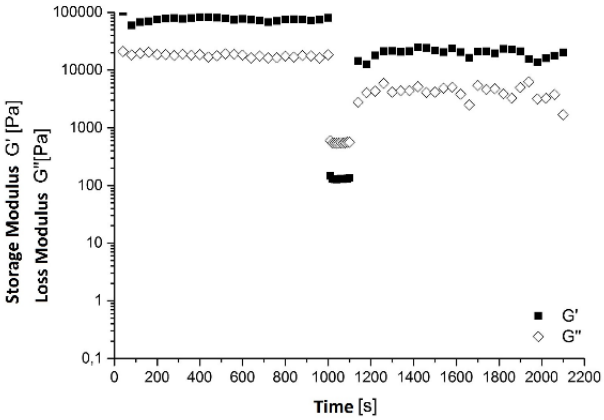

Figure 3. Step test.

Wet Film Thickness. Before the implementation of a measuring device the wet film thickness was adjusted by eyesight. The dependency on the resolution was observed when using a slurry formulation without light absorber. Fig. 4 shows the digital part geometry expressed as an STL-file (standard triangulation language). The desired diameter and height of the cylinder were 10 mm.

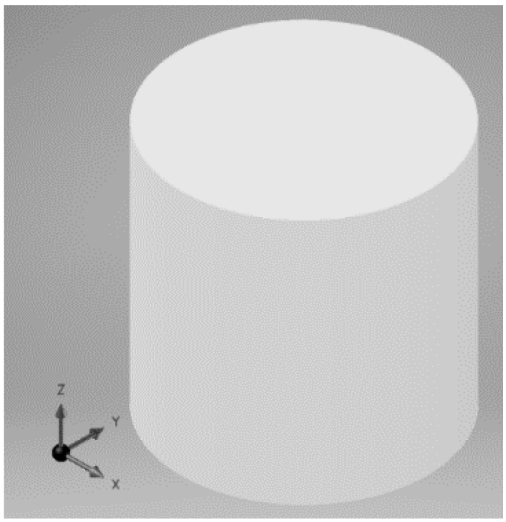

Figure 4. Portrayal of the STL-file of the desired Cylinder.

By adjusting the wet film thickness, the difference in dimensions between the STL-file and the printed green part could be increased or decreased at will as Fig. 5 shows. The corresponding dimensions are given in Table 2.

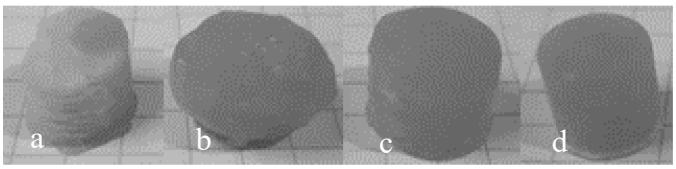

Figure 5. Four cylinders, each printed with different wet film thicknesses.

Table 2. Dimensions according to Fig. 5.

Cylinder	Diameter (mm)
a	10.15
b	14.39
c	12.57
d	10.22

Following this observation, several adjustments to the coating system were made, to enable a reproducible wet film thickness with a high quality, i.e. even and smooth.

Changes to the Vat. To this moment vats for the Blueprinters were build using a borosilicate glass plate on which a silicone layer was cast manually. To facilitate this step, silicone was replaced by an anti-adhesive layer of fluoropolymer with thicknesses of either 200 µm (F200) or 800 µm (F800), respectively.

Since the light exposure happens from below, i.e. through the transparent vat, a thinner layer has many advantages. The polymeric material is partly crystalline, so the thinner layer transmits a higher light intensity. Additionally, the refraction index of F200 (nD20 = 1,40) is closer to the refraction index of borosilicate glass (nD20=1,47) than that of F800 (nD20= 1,34). Therefore the thin layer causes less deviation of the beam of light. This results in higher part resolution when using the same light intensity and exposure time respectively.

These anti-adhesive polymers also have a great influence on the establishment of thin continuous wet films. Biaxial bending plates printed using the vat coated with F800 show many macroscopic defects when the wet film thickness is adjusted below 250 µm. These are shown in Fig. 6.

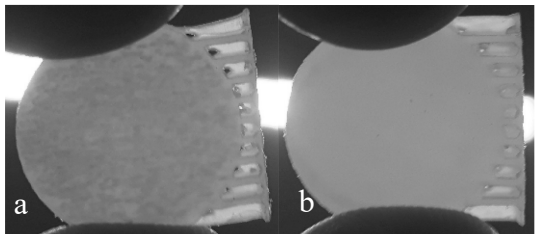

Figure 6. Biaxial bending plates printed with a wet film thickness below (a) /above (b) 250 µm.

A vat coated with F200 allows for a minimum wet film thickness of 150 µm without introducing defects to the green part. The reason for this is the wettability of the surface. F200 has a higher wettability because of its lower fluorine content.

Changes to the Doctor Blade. In the beginning, a rather simple doctor blade was used to determine the slurry coating process. The distance of the blade to the vat surface could be adjusted by two screws. Adjustments had to be done by eyesight and a measurement of the final wet film thickness was not implemented. First measurements showed. that usual wet film thicknesses were higher than 300 µm. The initial doctor blade is shown in Fig. 7.

To enable a reproducible adjustment a new doctor blade was designed by integrating the precision of manual stages.

In a circular vat, lower diameters have a lower surface area than bigger diameters. Therefore, during the coating process, the inside is coated with a thicker layer of slurry than the outside. To compensate this inequality a goniometer is also integrated which allows to adjust the gap height with regards to the vat diameter. The blade itself is made of PTFE (Polytetrafluoroethylene). Fig. 8 shows the new setup.

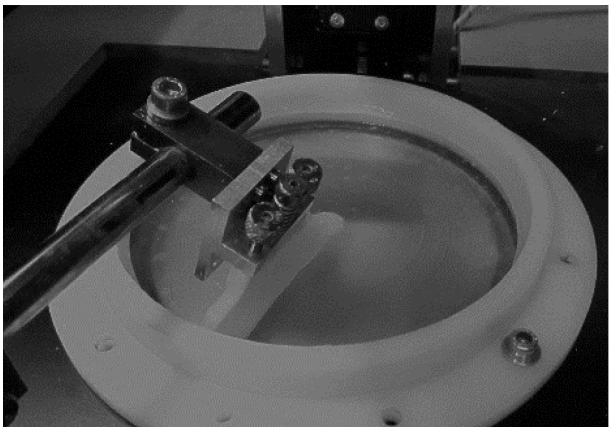

Figure 7. Initial doctor blade used in the *Blueprinter* 5.

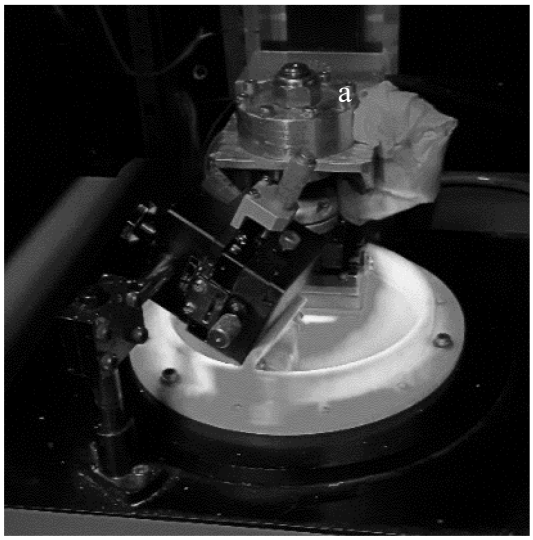

Figure 8. Newly designed doctor blade in the *Blueprinter* 5 during light exposure.

Changes to the Building Platform. Initially the building platform consisted of a roughened glass plate mounted on a metal frame. The roughening was performed to increase the surface area in contact with the first cured layer and thereby increase adhesion to the building platform. Additionally several LEDs on a metal template were inserted in the metal frame to enable a back light exposure, which also supports the adhesion.

Experiments showed that this sort of building platform leads to backscattering, which decreases the accuracy of parts. For this experiment so called "Siemens stars" were built and it was visible that the accuracy gradually increases with the progress of printing. Fig. 9 shows the old building platform together with the backside of the Siemens star that was printed on it.

Therefore, adjustments were made to decrease the amount of backscattered light. In a first trial experiment, the back light device was removed and the glass plate was covered with a black tape from the inside. This way, significant improvement of the part accuracy could be achieved. Fig. 10 shows the adapted building platform together with the backside of the Siemens star that was printed on it.

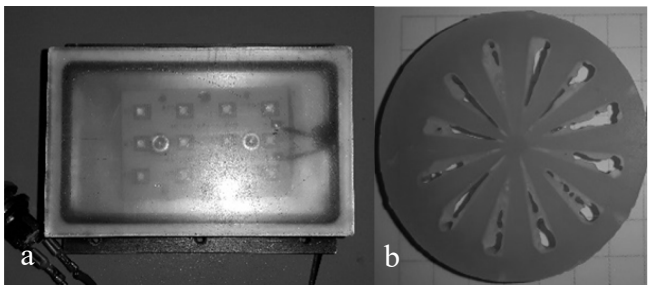

Figure 9. Old building platform (a) and the backside of the Siemens star that was printed on it (b).

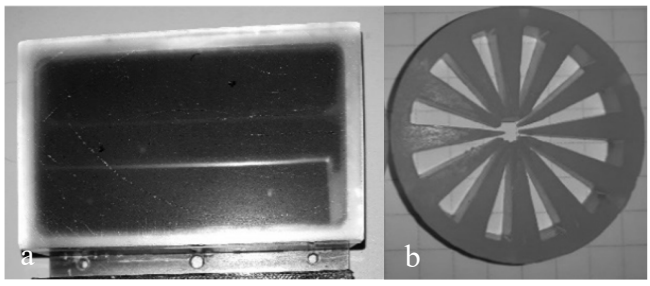

Figure 10. Adapted building platform (a) and the back side of the Siemens star, that was printed on it (b).

This discovery lead to a new design of the building platform, which is shown in Fig. 11. The metal frame was replaced by a closed, black polymer mount, on which an orange glass plate was bonded by using a 2-component epoxy glue.

Figure 11. Newly designed building platform of Blueprinter 5.

Biaxial Bending Strength. Including the described changes, biaxial bending test plates were printed according to the orientation shown in Fig. 12. A layer height of 50 µm was chosen. 15 specimens were prepared this way. They were debinded, sintered and tested 'as fired', i.e. without further grinding or polishing steps. The force necessary to break them was recorded and the bending strength calculated. The Weibull strength and modulus were determined. Finally, a Weibull-strength of 338 MPa was reached with a Weibull-modulus of 10 according to Fig. 13.

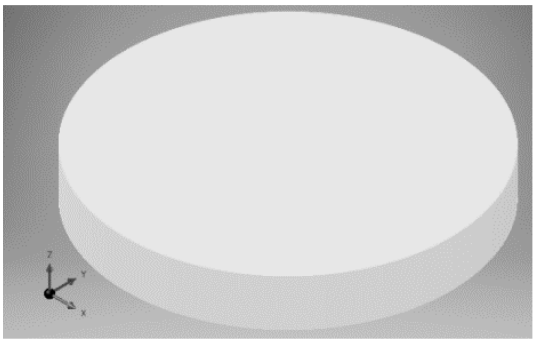

Figure 12. Portrayal of the STL-file of a biaxial bending test plate.

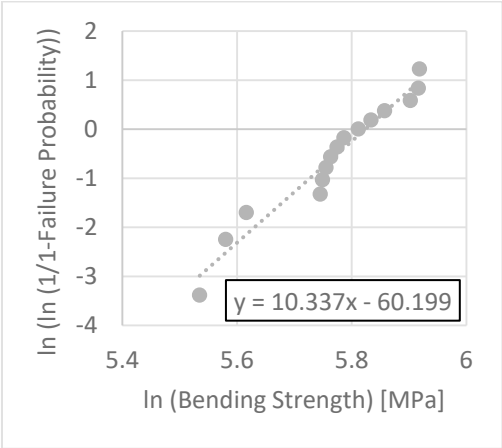

Figure 13. Determination of the Weibull-Modulus.

Accuracy of Sintered Parts. Siemens stars proved to be a practical tool to evaluate the accuracy of printed parts quickly and comparably. Fig. 14 shows the STL-file as the target geometry.

Fig. 15 shows the sintered parts, that were produced via LCM including the described changes. The diameter of both stars is 18.0 mm and the height is 3.2 mm.

By reducing the wet film thickness and therefore the overall excess amount of slurry, a cleaning step after green part production is nearly redundant regarding part accuracy, as we can see by

comparing the cleaned and the uncleaned parts. Cleaning is done by thoroughly rinsing with water. The green bodies have been manufactured using a wet film thickness of <100 µm.

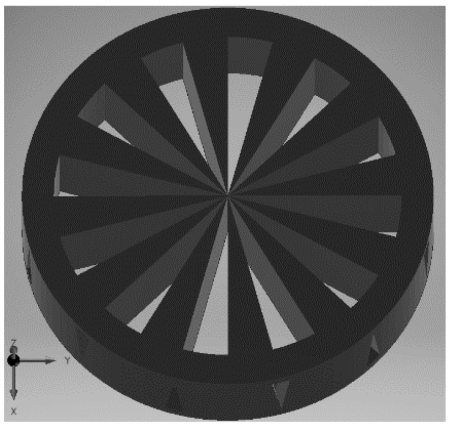

Figure 14. STL-file of a Siemens star.

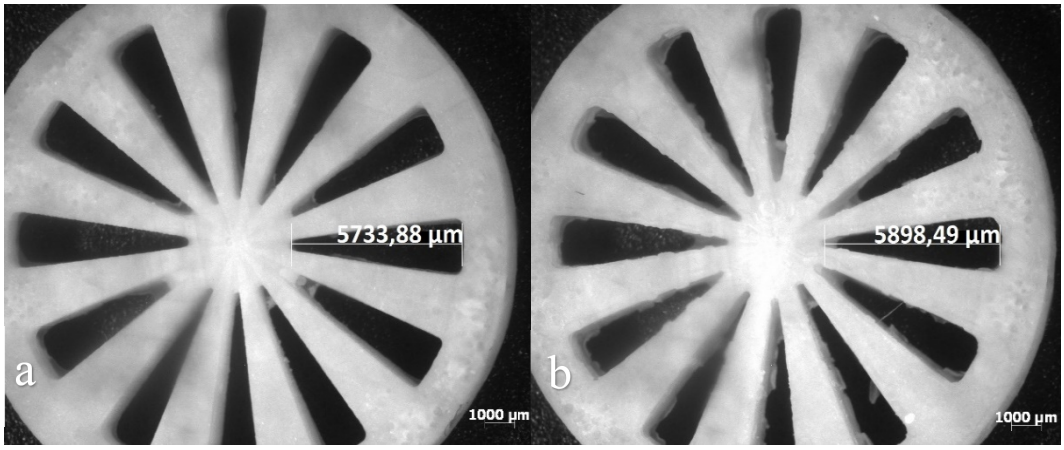

Figure 15. Sintered Siemens star, cleaned (a), fired as printed (b).

Discussion

Sedimentation during the printing process or during down time is problematic because it can lead to jamming of the doctor blade. This is why slurry stability is one of the basic requirements in LCM. With the shown formulation we were able to provide a slurry that is stable during printing and over usual down times, which can be hours or days in single cases up to weeks.

The wet film thickness could be identified as an important parameter regarding part accuracy. Therefore several changes to the machine setup were made. As a change to the vat design, F200 proved to be the preferred choice, because it is commercially available as a thin self-adhesive tape. Laminating a glass plate is therefore very simple and in the case of damage it can also easily be removed and replaced. Additionally, lower wet film thicknesses can be established when compared to F800.

Changes to the doctor blade enabled a reproducible setting of the wet film thickness and at the same time, allowed to equalize the uneven coating thickness due to the circular vat design.

By removing the dye in the slurry formulation, which acts as a light absorber to stray light caused by ceramic particles, a severe influence of the wet film thickness to the accuracy of printed parts could be observed.

Light absorber is generally used to decrease the penetration depth of curing light and thereby increases the Z-resolution during the printing process. At the same time, with light absorber, a higher exposure energy is needed to achieve the same green part strength. A higher exposure energy is equivalent to longer exposure duration when using the same light intensity. Since short exposure durations are always favorable, when it comes to building speed, a minimum of light absorber

concentration should be added. With the described changes to the machine setup, which allow to minimize the wet film thickness, another possibility to decrease the penetration depth was shown.

We could see, that the material choice and quality of the building platform strongly influence the part accuracy. With the adaptations made, inaccuracies due to reflections could be avoided.

As a final quality criterion for additively manufactured ceramic parts, biaxial bending tests were chosen. The value of 360 ± 60 MPa for CAD/CAM produced IPS e.max [4] acted as a reference. With a Weibull strength of 338 MPa, it is fair to say that comparable values can be achieved by LCM.

Conclusion

By considering the criteria discussed in this text, we were able to additively manufacture parts made of the lithium-disilicate glass-ceramic, which is widely used in dentistry.

Performing several adjustments to the machine enabled us to process a highly viscous slurry, which can be regarded as stable over considerable storage times. At the same time, parts show exceptional quality regarding accuracy, even when not cleaned after green part production.

This is due to reducing the wet film thickness, which could be identified as a major influencing factor, when producing ceramic parts via stereolithography.

When it comes to the material properties of final parts, we reached a biaxial bending strength that is comparable to those produced by CNC-milling.

To further increase the bending strength and part accuracy at the same time, finding a suitable vat coating material, which enables lower wet film thicknesses without introducing defects during green part production, is a task for future work.

Acknowledgement

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