IN-PROCESS UV-CURING OF PASTY CERAMIC COMPOSITE

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Abstract

Within recent years,a wide range of additive manufacturing processes have been developed. While powder bed based fusion processes like selective laser melting and melting processes like fused layer modelling are being increasingly used in industrial applications, prototyping other processes are in the initial stage. This paper develops a new method for an extrusion-based process of pasty UV-curing ceramic composite material. The method proposes an approach to continuously cure the material while it is deployed to reduce process time and generate complete cured parts. A milling machine has been modified with a syringe and a UV-light source to accommodate the process. Experimental studies have been carried out to examine the influence of the process parameters on the curing process. As a result, a parameter set has been found to make fully dense and cured ceramic composite parts.

Introduction

Additive manufacturing (AM) processes are currently the base for a variety of research projects. This emerging field in manufacturing technologies functions on the common principle of building up solid parts directly from 3D-CAD data by adding material layer by layer. Metal, plastic, ceramic or, as expected in the future, human tissue, can be used in AM. Particularly in areas like medical and dental technology, extensive requirements are placed on the production processes and resulting products. Using new production processes, the main goal is to match the specific material properties in the conventional production process. This is possible through the controlled use of a variety of process parameters. Stereolithography is the state-of-the-art in the field of AM of UV-curing ceramic composites. However, this process can only be used on flat surfaces so that it is currently not possible to print on freeform surfaces. Therefore, a new process must be developed to apply pasty material onto freeform surfaces. Precautions must be considered in order to stabilise the location of the material application and to prevent the material from running.

This paper investigates the in-process UV-curing concept for an extrusion-based 3D printing process of pasty ceramic composite. To do so, a state-of-the-art conventional UV-curing process within a UV oven is investigated and critical factors are identified. Adjusting the hardware setup, the process is then ready to be transferred into a different environment in the form of an extrusion-based 3D printer. The influence of critical factors is examined and process parameters are adjusted with a focus on reaching the same surface hardness as the curing process within a UV oven.

The UV-curing process of composites themselves has been studied for years so that many interactions of individual process parameters are known. However, these have yet not been investigated for curing during an extrusion-based material application. For this purpose, the interactions must be re-examined and assessed from the perspective of the overall process.

State-of-the-art

Many correlations of process parameters of the curing process have already been outlined in studies. It has been shown that there is a partially linear relationship between the surface hardness of the cured ceramic composite and the light intensity used. However, this linearity only applies to a limited area [1]. A reduction of the light intensity used can be compensated by an increase in the exposure time [2]. Another insight is the decreasing hardness depending on the material depth or sample height. This can be explained by the absorption of light entering the translucent material. For this purpose, a model was created, depending on the depth of cure, light intensity and curing time. However, due to a maximum achievable surface hardness, the model can only be used in a limited range [3]. In a further study to determine parameters relevant to the curing depth, in addition to the curing time and the light source, the material composition was also identified [4]. It turned out that in all examined composites, the depth of cure remains almost constant to a certain depth, between about 0.5-5 mm at a lighting duration of 300 s and then decreases rapidly. It has also been shown that as the illumination duration decreases, the cure depth decreases as well, and that the proportion of starters in the different composites is crucial for the curing depth. In [5], the material composition, the light intensity of the light source, the curing time and the distance between the tip of the light source and the body to be cured were identified as the four crucial factors of the curing process. In addition to the affirmation that lighter and more translucent materials allow a greater hardening depth under the same conditions, the result was a correlation with increasing distance from light source to the body to be cured. As the distance increases, a significant reduction in polymerisation occurs at >20 mm. To determine the influence of the light source, [6] compares conventional halogen lamps with an LED light source. Both achieve a more than sufficient hardening depth.

Research methodology

VITA VM LC flow (Enamel), a commercially available ceramic composite for the top layer of dental applications, is used as raw material to conduct the experiments. In dental laboratories, a dental technician manually applies the material according to the processing instructions given by the material manufacturer VITA Zahnfabrik H. Rauter GmbH (VITA). The part is than placed in a VITA recommended UV oven for the UV-curing process to reach its necessary surface hardness of > 60 HV0.5. In this study, the bre.lux Power Unit 2 UV oven is used. This curing process serves as a reference during the experiments. The light source in the UV oven contains 72 LEDs, the exact type and wavelength spectrum of which is unknown. The ceramic composite Enamel consists of an organic matrix, a disperse phase and a composite phase. Monomers, in this case, di-acrylates, form the organic matrix which react with one another by radical polymerisation and cure. To start the curing process, the organic matrix is enriched with two initiators:

- Kampherchinon with an initiating wavelength of 468 nm
- TPO with an initiating wavelength of 380 nm.

Colour pigments are another ingredient, but just for cosmetic reasons. The disperse phase consists of silica and zirconium dioxide. These are responsible for hardness and polishability after curing. The composite phase represents the functional connection between organic matrix and disperse phase.

As none of the above studies deal with the ceramic composite Enamel used here or with the goal to integrate the curing process into an AM process, the individual factors must be considered again.

The curing process with the oven used fulfills the requirements of DIN EN ISO 10477:2017 [7]. To better understand the process, hardware components of the oven are examined. Here, the wavelength spectrum of the LEDs used and the light intensity over time are of particular interest. The LEDs of the oven use the wavelengths 380 nm and 468 nm to initiate the hardening process of Enamel. Because the LED wavelength bandwidth is narrow in comparison to other light sources, it is assumed that intensity peaks are close to these initiation wavelength [8]. To carry out the wavelength measurement, a hand spectrometer, a pulse generator, a specially designed mounting box for the LEDs and optical Mirror and filter are used and arranged according to Figure 1. The LEDs of the UV oven are mounted in groups of three on PBC printed circuit boards. One printed circuit board is placed in a specially made box, which allows the shielding of the individual LED light beams, whereby the control technology of the UV oven for driving the LEDs could continue to be used. In order to take the temperature dependency of LEDs into account, the measurement was carried out over 720 sec, the reference time specified by VITA. Therefore, the control technology of the UV oven runs an internal programme of 360 sec twice.
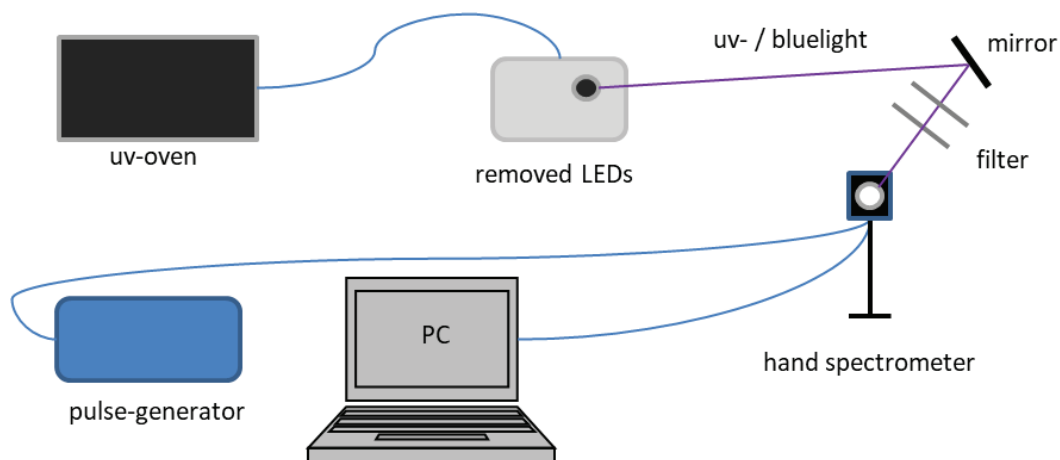

Figure 1: setup for the measurement of LED wavelength spectrum

In a further step, the light intensity is measured over the reference time of 720 sec. The maximum light intensity is selected to achieve maximum curing and curing depth during the limited curing time. For this measurement, it is important to keep the functionality of the oven's LED control intact. By constantly introducing energy into the body, the temperature also has influence on the curing process. In the Enamel data sheet [9] has described that a temperature range between 60 °C and 80 °C is beneficial for the polymerisation.

In order to implement a curing process into a 3D printer, a light source has to be available inside the interior of the printer. For this purpose, a holder for numerous LEDs is developed in which different LED types can be installed. In order to create a possibility for transporting the light from the source to the body, the PURAVIS® GOF70 light guide from SCHOTT AG is used for the required wavelengths due to the transmission rate. With this hardware setup, preliminary tests are carried out. In these tests, the surface hardness of the top, the bottom and the ratio of these two are measured and compared. These represent the quality feature according to which the quality of the process can be assessed. For comparison, the experiment is also carried out in the UV oven.

The test body is manufactured manually according to DIN EN ISO 10477:2017 [7] specifications. The test body is a 1 mm thick disc with a diameter of 15 mm. The hardness measurement on the surfaces is carried out after Vickers.

An LED pairing of suitable wavelengths, the influence of the light intensity, the curing temperature and the number of light sources are examined in respective test series. The post-curing time, the time after the LEDs turn off until the surface hardness is measured, is standardised to 20 min because of results reached in [10]. Here, no significant differences in surface hardness are shown in the time windows between 20 and 60 minutes or one and seven days post-curing. The results obtained are used to draw conclusions on how a further optimisation can be designed to reduce lighting time and therefore the curing process time. The main objective is to achieve the same or better component properties, so it is sufficient to look at the process qualitatively. Since the curing is taking place as a radical polymerization, it needs to be considered that this is a chemical reaction over time. All experiment are carried out in an air-conditioned measuring room.

Process development

The process development is carried out to estimate the potential of the UV-curing process for integration into an extrusion based additive manufacturing process. Therefore following investigations of the curing process and critical process parameters are made:

- Measurement of the wavelength spectrum and radiation intensity
- Measurement of surface hardness over lighting time
- Measurement of surface hardness over different wavelength
- Measurement of surface hardness over operating current
- Measurement of surface hardness over curing temperature
- Measurement of surface hardness over lighting time of preheated sample

Measurement of the wavelength spectrum and radiation intensity

The results of the wavelength measurement in the UV oven show that three different types of LEDs are installed. The wavelength peaks of the three LED types are at 450 nm, 459 nm and 395 nm, as shown in Figure 2 a-c. Figure 2 d shows the wavelength spectrum of all three LEDs put together. Here, the wavelength to trigger the initiators for the curing process, Kampherchinon (468 nm) and TPO (380 nm), are also marked in the graph. It is shown that the intensity peaks of the used LEDs do not align with the initiator wavelengths. This indicates the potential for optimisation through the use of more suitable LEDs in which the intensity peaks are at the initiator wavelengths. Based on these results, a larger wavelength range is covered in the later LED selection with the attempt to ensure optimised performance.

A second result of the hardware setup is the radiation intensity of the LEDs. It can be concluded from the results that the lighting in the oven runs a specific internal programme. The radiation intensity starts with a jump to 50% of the possible power, is held there for about 30 s, and then increases linearly to 100% intensity. A slightly decreasing radiation intensity after approx. 80 sec is due to thermal effects within the LEDs themselves, as they show decreasing efficiencies with increasing temperatures. From 180 sec, the modulation programme of the UV oven begins with a variation of the radiation intensity between 50% and 100% for intervals of a few seconds.
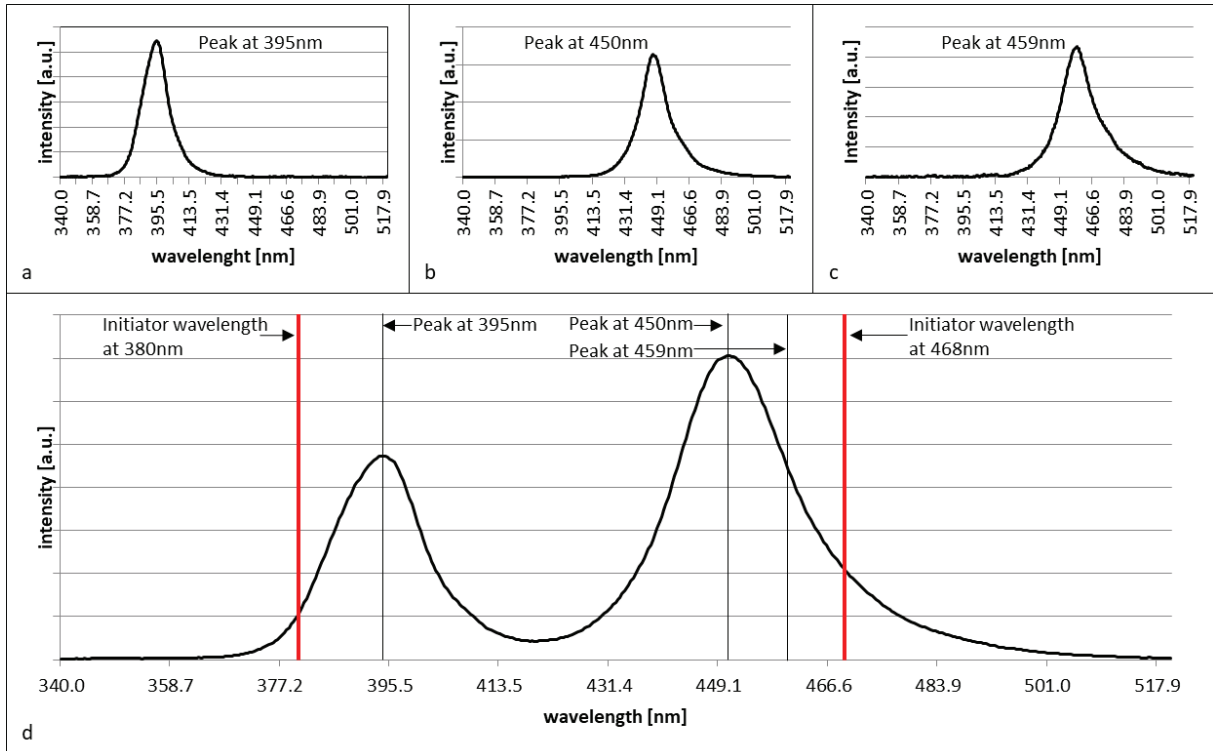
Figure 2: a-c) wavelength spectrum of the three different LEDs used in the uv-oven; d) combined wavelength spectrum of all three LEDs used in the uv-oven and marking of the qualitative intensity of the initiator wavelength

Measurement of surface hardness over lighting time

For the development of a new curing process, a test setup is designed. In this setup, the variable combination of same or different LEDs is possible. A base body is designed to hold up to ten LEDs while ensuring sufficient heat dissipation for the LEDs. An upper body serves as a carrier of the light guide and is fitted appropriately. To carry out the experiment, individual LEDs are fastened in the base body and connected to a power source and a controller. The ends of the light guides are positioned 20mm above the samples to be cured, as shown in Figure 3.
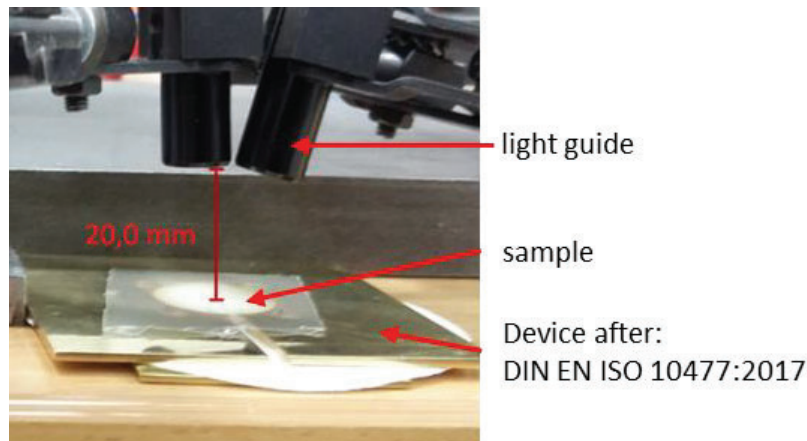

Figure 3: test sample with the light emitting end of the light guide

During the experiments, LEDs with wavelength peaks shown in Table 1 will be used, where twice-occurring wavelengths differ by different power and technical specifications:

Table 1: List of LEDs and wavelength used

UV LED		blue LED	
Name	wavelength	Name	wavelength
LED A	370 nm	LED E	445 nm
LED B	385 nm	LED F	458 nm
LED C	395 nm	LED G	458 nm
LED D	395 nm	LED H	470 nm
		LED I	475 nm

In the first series of experiments, the lighting time t_B is varied between one and twelve minutes. The LED pair consisting of the UV LED B and the blue LED I was operated with a current of 0.5 A. The graph in Figure 4 shows that, from an exposure time of more than 5 minutes, no significant influence on the total hardness H_G was observed, taking into account the standard deviation. In order to exclude the lighting time as an influencing factor in the following series of experiments, lighting time t_B is set to six minutes. The experiment is repeated with other LED pairings and show similar results.
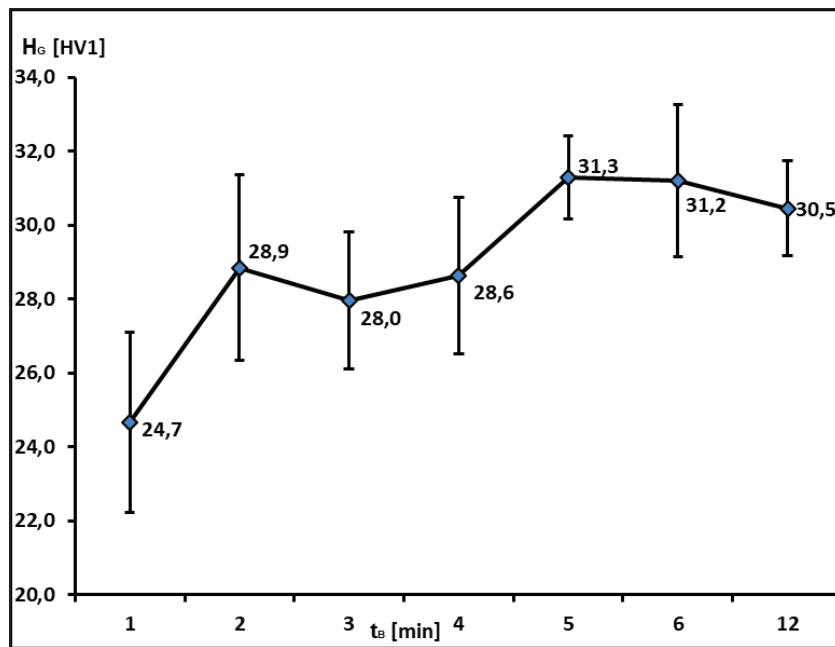

Figure 4: Total hardness H_G over the lighting time t_B, LED pairing B & I, current $I_B = 0.5$ A, post-curing time $t_h = 20$ min, curing temperature $T_A = 21$ ° C, number of LEDs n = 2

Measurement of surface hardness over different wavelength
To achieve a process in which the two initiators are triggered optimally, the LEDs are paired with each other, consisting of a UV LED and a blue LED. The goal is to find a combination that is particularly suitable for the process. For the experiments a lighting time of six minutes, a current of 0.5 A, and a post-curing time of 20 minutes are used. The 20 possible LED pairings are examined

and the surface hardness of the prepared samples is measured at six points, three at the top and three at the bottom. The results are shown in Figure 5. Regardless of the influence of the five blue LEDs, the two UV LEDs A and B appear more suitable for the curing process than the LEDs C and D, since the achieved average surface hardness is higher. A statement about a specific blue LED could not be made with this measurement series because whether the results have a big range, e.g. LED E from 28 to 33.3 HV1, or the values are in too low a range, e.g., LED I from 29,6 to 31,2 HV1, additional iterations are necessary.
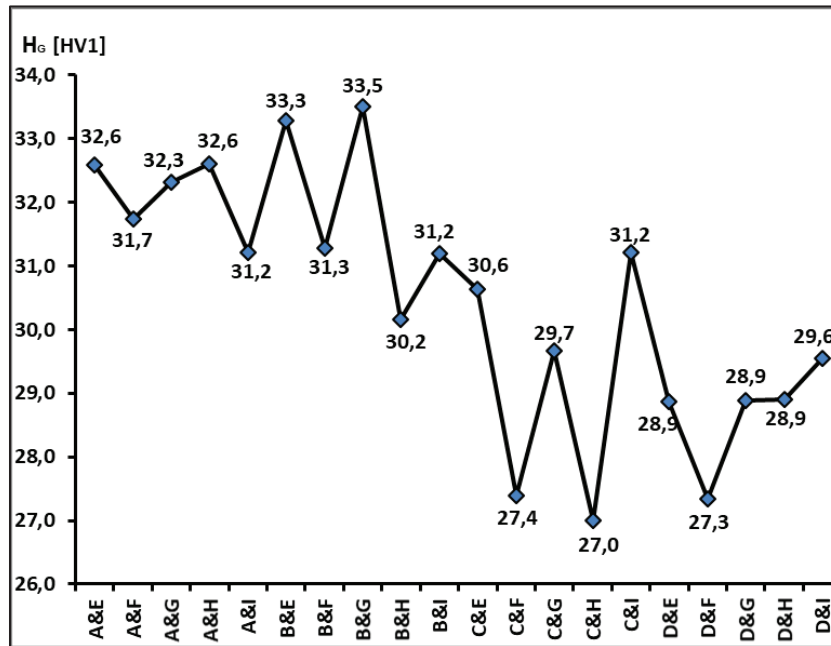

Figure 5: Total hardness H_G of twenty LED pairs, lighting time $t_B = 6$ min, current $I_B = 0.5$ A, post-curing time $t_h = 20$ min, curing temperature $T_A = 21 °$ C, number of LEDs n = 2

Measurement of surface hardness over operating current

The radiation intensity of the light sources is examined as an influencing factor to the curing process. By varying the operating current, the radiation intensity is adjusted. These are in an approximately linear correlation to each other [11]. The temperature of the LEDs is kept constant during the experiments by active cooling. As a result, a decrease in the efficiency by increasing temperature [11] is prevented. For the experiments, the LED pairing B and I is used with a lighting time of six minutes and a post-curing time of 20 minutes. The operating current is varied in a range from 0.06 A to 1 A. The resulting graph is shown in Figure 6. Here, no significant differences for the surface hardness are shown in a corridor of the operating current I_B between 0.25 A and 1 A. The surface hardness decreases strongly below an operating current of 0.25 A, from 29.5 to 27.3 HV1 within a range of 0.125 A. Than sharply from 27.3 to 20.8 HV1 within a range of 0.06 A. As a result, the operating current IB is maintained at 0.5 A for the further factor variations.
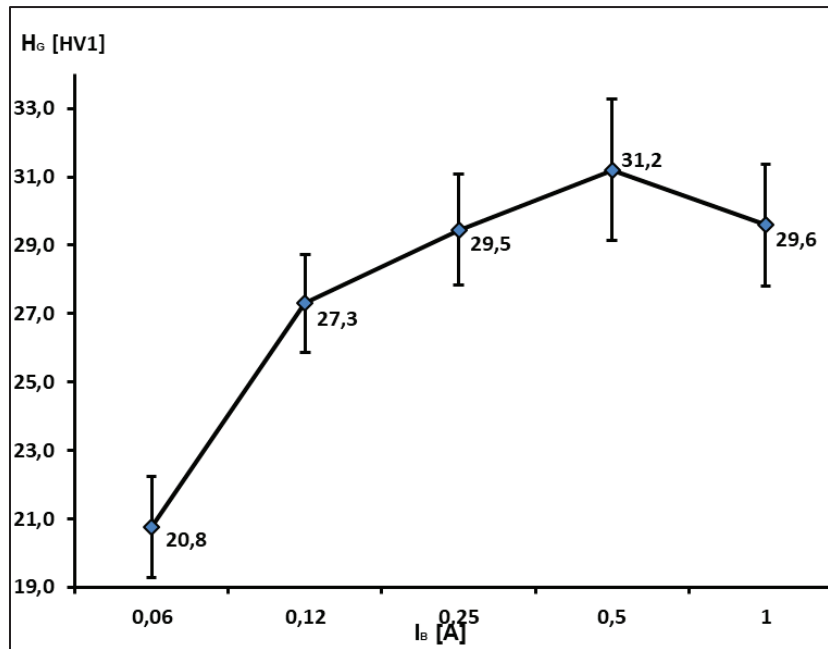
Figure 6: Total hardness H_G as a function of the operating current I_B, LEDs B & I, lighting time t_B = 6 min, post-curing time t_h = 20 min, curing temperature T_A = 21 ° C, number of LEDs n = 2

Measurement of surface hardness over curing temperature

The curing temperature T_A is examined as an influencing factor. For this experiment, a new hardware setup is created that allows it to vary the temperature of the test body before the curing process. Otherwise, the experimental conditions, e.g., distance between test body and light guides, are kept constant. Because the experiments for determining a suitable LED pairing at room temperature did not provide a clear statement, they are repeated in parts. For this purpose, all four UV LEDs were combined with one LED each at the lower and upper blue wavelength spectrum, the LEDs E and I. The results of the first series of measurements at a curing temperature T_A of 60 ° C, a lighting time t_B of 6 min, a post-curing time of 20 min, and an operating current I_B of 0.5 A are shown in Figure 7. It draws the conclusion that LED B has the best suitability for the process, with a surface hardness of 64 HV1. The desired reference surface hardness of > 60 HV1 is achieved for the first time during the entire experiment procedure.
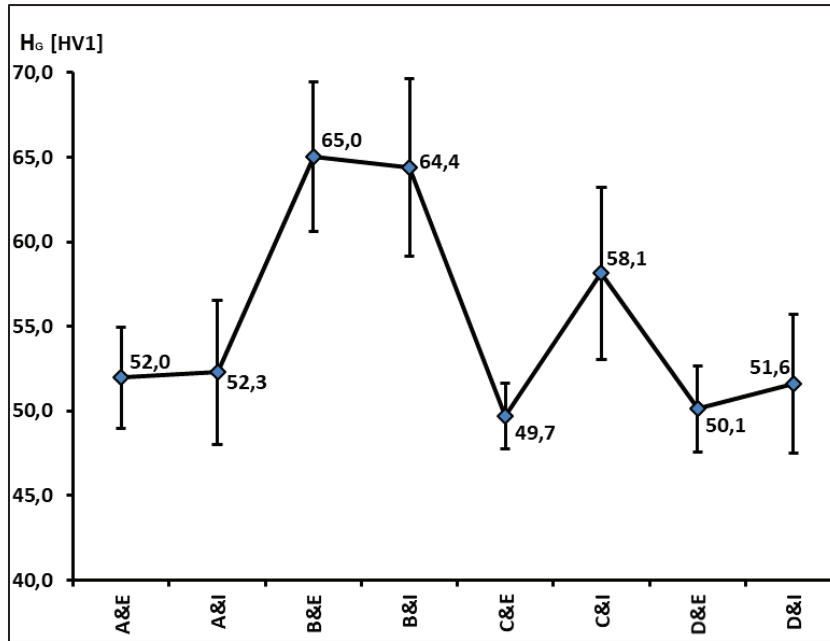
Figure 7: Total hardness H_G of eight LED pairings, lighting time t_B = 6 min, current IB = 0,5 A, post-curing time t_h = 20 min, curing temperature T_A = 60 ° C, number of LEDs n = 2

LED B is chosen for the UV range for further testing. Therefore LED B is combined with all blue LEDs and the experiment is repeated with the results displayed in Figure 8. The graph shows that the results of the pairing B & E (49.2 HV1) and B & I (54.9 HV1) deviate from the results of the previous test series (B & E = 65 HV1; B & I = 64 HV1). This deviation can be attributed in part to a shorter warm-up phase of the test bodies. By reaching a new maximum surface hardness of 66.9 HV1, the LED pairing B & F is selected for further tests.
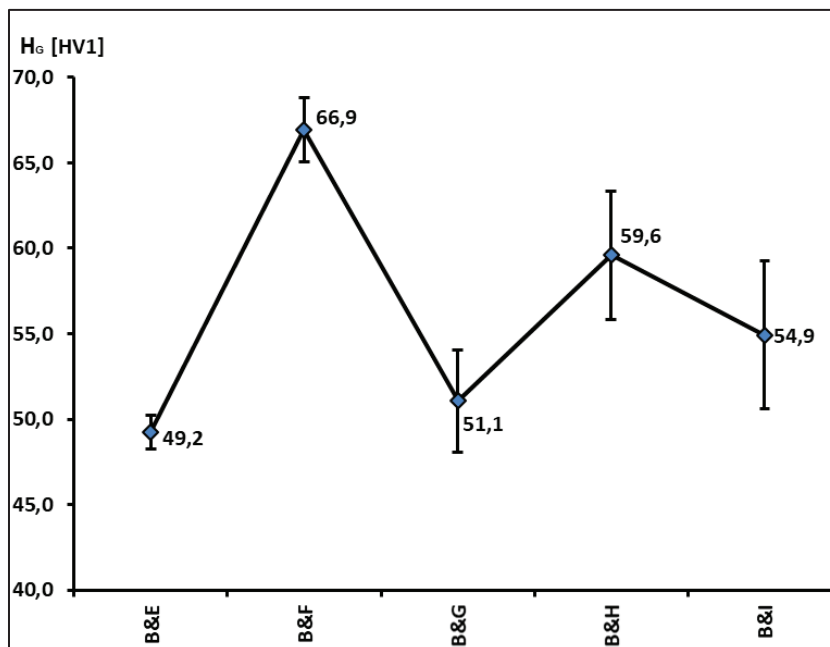

Figure 8: Total hardness H_G of five LED pairings, lighting time t_B = 6 min, current I_B = 0,5 A, post-curing time t_h = 20 min, curing temperature T_A = 60 ° C, number of LEDs n = 2

In order to validate the results, further test series were carried out which are not considered in detail. As a conclusion of these experiments, it can be stated that, above all, the temperature increase has a decisive influence on the achievement of the surface hardness of the reference process. Therefore, the focus is on the influence of the curing temperature T_A in the following step. The temperature T_A will be varied between 21 °C room temperature and 60 °C and a preheating time of t_V of 6 min for the test body is set. As shown in Figure 9, the resulting surface hardness H_G decreases exponentially as a function of the curing temperature T_A from 64.7 HV1 at 60 °C to 27.3 HV1 at 21 °C. This underlines the cure temperature T_A being the strongest process factor so far.
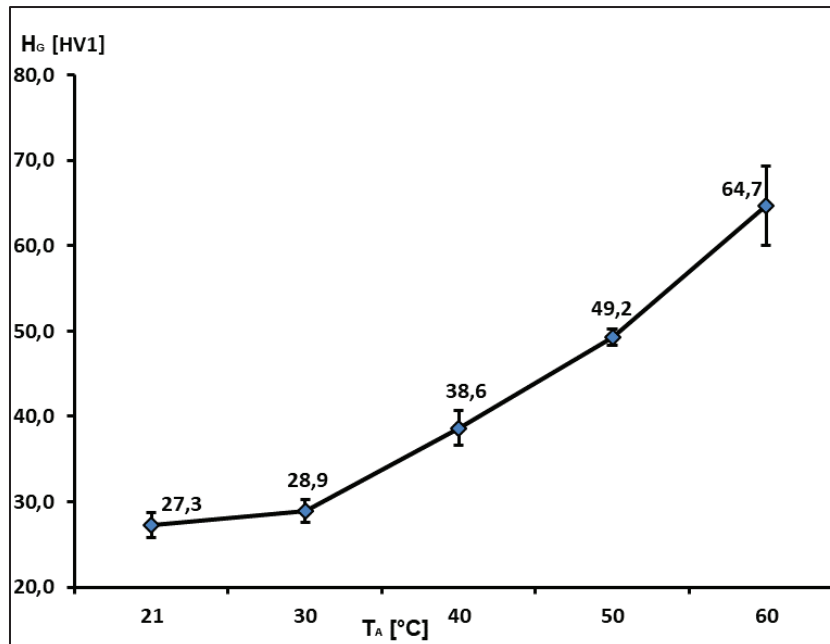

Figure 9: Total hardness H_G of the LED B&F as a function of the curing temperature T_A, lighting time t_B = 6 min, current I_B = 0,5 A, post-curing time t_h = 20 min, number of LEDs n = 8

Measurement of surface hardness over lighting time of preheated sample

Having found the appropriate light source constellation LED B & F, examined the influence of radiation intensity I_B and the curing temperature T_A, and after increasing the number n of LEDs, one more step to identify the possibility of an inline curing process is to minimise the lighting time t_B. In this experiment, the test body is preheated for t_V = 6 min and removed from the heat source directly after lighting time. The curing temperature was increased to 70 °C. The resulting graph in Figure 10 shows a lighting time of two seconds and a surface hardness of 46.1 HV1. After 30 seconds, a hardness of 68.5 HV1 is measured and represents a maximum value in these experiments. The value set by the reference process > 60 HV1 is measured after a lighting time of 8 sec. Furthermore, a sample was heated at 70 °C for six minutes without exposure to a lighting process. Even after a waiting time of 20 minutes after the process, the composite was still pasty.
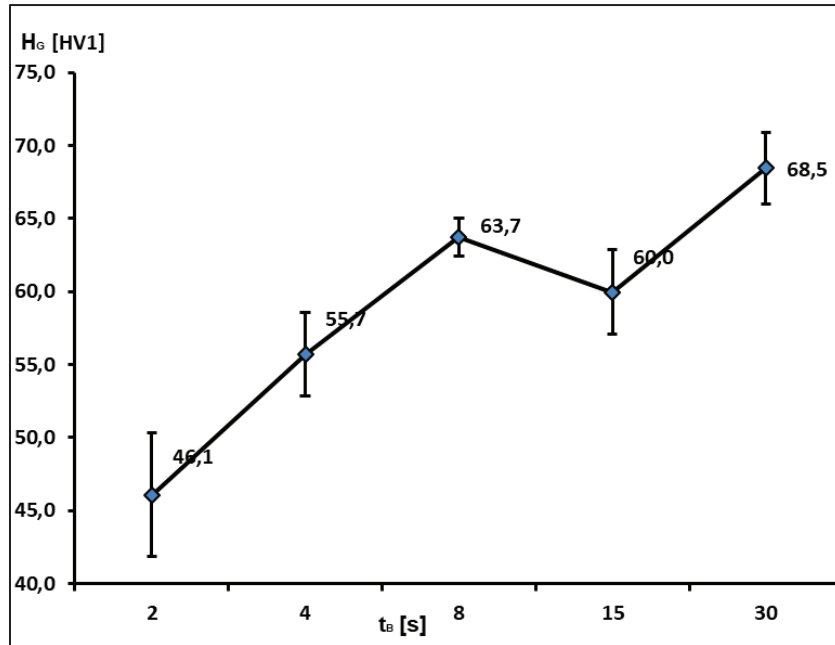
Figure 10: Total hardness H_G of the LED B&F as a function of the lighting time t_B, preheating time $t_V = 6$ min, current $I_B = 0,5$ A, post-curing time $t_h = 20$ min, curing temperature 70 °C, number of LEDs $n = 8$

Discussion

The wavelength measurement results conclude in a potential for optimisation of the curing process in terms of curing time. The limited number of wavelengths considered in LED selection offers room for further optimization and use of more appropriate wavelength LEDs is a first conclusion to be drawn. In contrast, a reason for the temporal modulation of the radiation intensity remains unclear. It could promote the curing process, regulate the process temperature by regulating the energy input, or reduce the thermal load on the LEDs and the printed circuit board. Following the steps taken to determine the critical factors of the curing process and the additionally investigated factor preheating time t_V, the following factors are listed in Table 2.

Table 2 : Critical factors for the curing process

Critical Factor	**Symbol**	**Range**	**Unit**
Wavelength	λ_{UV} und λ_{Bl}	385 (B) & 458 (F)	[nm]
Number of LEDs	N	2 – 8	-
Operating current	I_B	$\geq 0,5$	[A]
Lighting time	t_B	8 – 360	[s]
Curing temperature	T_A	60 – 70	[°C]
Preheating time	t_V	0 - 360	[s]

The first factor, the wavelengths λ_{UV} and λ_{Bl} respectively the LED configuration of the process, is consistent with the spectral absorption peaks at 380 and 468 nm of the two photo-initiators Lucirin TPO and Kamherchinon used in Enamel. Individual LED characteristics and manufacturer-dependent quality differences of the luminous efficacy at the same operating currents I_B could influence the results. There is no significant difference in the total hardness H_G of the

samples correlating with the number of LEDs n. A negative influence of a higher number of LEDs on the curing process is excluded, but a reduction in the number of light sources could make sense in the context of a cost-effectiveness analysis of the overall process. The operating current I_B and the radiation intensity of the LED light sources proved to be sufficient, starting from a value of 0.5 A. A further increase of these could neither accelerate the hardening process nor achieve better hardness values. The determination of a more exact threshold of the operating current may be economically viable for the continuous operation of a 3D printer. The lighting time t_B can be selected depending on preheating time t_V and hardening temperature T_A between eight and 360 seconds, with a correlation of these three with each other. Thus, the UV and blue light radiation entry into the material proved sufficient after a lighting time of 8 sec, implied that a curing temperature T_A of 70 °C and a sufficiently high preheating time t_V is selected. This result suggests, that the 12 min lighting and curing time of the reference process is decreased by almost 99% down to 8 sec with comparable surface hardness value. It is safe to say that the reference process incudes a safety factor to ensure high reliability. A safety factor has not been included in the new process. The preheating time t_V is also a limiting component. If the sample to be cured is not heated sufficiently, the curing process and thus the lighting time t_B take longer, which results in a longer heat input. Since, during these experiments, the highest examined curing temperature was 70 °C, it is unclear how the curing process reacts to a further increase in temperature. However, according to the product data sheet of the manufacturer Vita, it should not exceed a temperature of 120 °C. Other problems in the process handling may occur if the curing time is too short and the curing process is thereby too fast. For example, the deposition process of the material to the surface be negatively influenced at the nozzle where the material is exposed to the light for the first time. The material behavior during a dynamic movement of an extrusion based AM process within a machinery needs to be examined. The influence of the deposition strategy considering parameters such as nozzle diameter, travel speed and volume flow will increase the process complexity. The transferability of the results with standard test specimens to individually deposited strands must be evaluated and can not be considered as given.

Summary and outlook

In this work, the key process parameters for an inline curing process within a 3D printing process are determined. An approved reference process is examined and a hardware setup is developed, which offers the possibility to be integrated into machinery. The dependencies of various process parameters among each other could be specified qualitatively. In particular, the curing temperature, the lighting time, and a possible preheating time of the body to be cured play significant roles in the process. The overall hardness, as the average surface hardness of the top and bottom of the specimen, is suitable as a quality standard for the evaluation of curing processes. The lighting and curing time 12 min of the reference process is decreased by almost 99% down to 8 sec with comparable surface hardness value.

Sustainable potential for further optimisation is provided by the three parameters illumination time, curing temperature, and sample preheating time. They all have significant effects on the curing process and influence each other during the process. With the need of further examinations, it is still unclear which technology can optimally ensure a constant curing temperature in this AM process or how a specific preheating can be implemented and what impact this has on the body. These aspects for optimisation need to consider the dynamics and parameters of an actual extrusion-based AM process.

Acknowledgements

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