CURING AND INFILTRATION BEHAVIOR OF UV-CURING THERMOSETS FOR THE USE IN A COMBINED LASER SINTERING PROCESS OF POLYMERS

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Abstract

The investigation in this study addresses a new additive manufacturing process, which enables the production of multi-material parts consisting of thermosets and thermoplastics. A liquid thermoset resin will be applied with a micro value syringe in the laser sintering (LS) system. The liquid thermoset reacts parallel to the laser exposure of the thermoplastic powder. Therefore, in this study the UV curing and the infiltration behavior of the thermoset will be investigated under process relevant conditions. The investigations show a strong temperature dependent absorption of the liquid in the powder bed, whereas, the surface tension of the liquid plays a minor role. Furthermore, the UV curing of the thermosets takes place at low interaction times and at lamp powers between 100 and 300 mW/cm².

Keywords: Laser sintering, thermoset, thermoplastic, multi-material part

Introduction

One trend in the field of additive manufacturing is to enlarge the applications of additive manufactured components. The range of application is limited due to the restricted material variety in powder and laser based additive manufacturing techniques. Although there are efforts to develop new materials for laser sintering (LS) [1-4], the availability of polymers that can be processed in LS is still very limited compared to conventional manufacturing methods like injection molding and only single materials can be processed. Despite polypropylene and thermoplastic elastomers are launched lately, Polyamide 11 (PA11) and Polyamide 12 (PA12) hold approximately 90 % of the market share in LS [5]. The low market volume of LS powders (900 tons/year) compared to the volume of total plastic production (260 million tons/year) in combination with the high development cost of LS decelerate the launch of new polymers for LS applications [5]. Nevertheless, there is a huge customer demand for new applications of additive technologies. The local adjustment of certain properties like mechanical characteristics, stiffness or hardness and thus the generation of multi-material parts could lead to significantly higher rates of usage of LS manufactured parts, because the achieved properties could cover more specifications. In this investigation, a new hybrid additive manufacturing technique is introduced, which could overcome the gap to create new features of additively manufactured components.
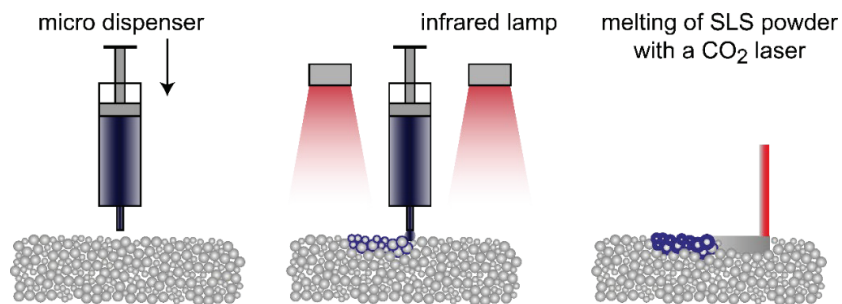
thermoplastic elastomer powder, is molten like in standard LS process with a CO_2 laser. Temporal the injection of the liquid can be done after of before laser exposure. The order of cross-linking and melting will lead to different boundary surfaces, which shall be investigated in further studies. After infiltration, cross-linking and melting a new powder layer is applied and the process steps start again. Like in laser sintering the thermoplastic material is cooled down after all layer are generated. The injection and curing of resins in LS process with parallel melting of the thermoplastic material lead to the generation of multi-material parts in one process.

State of the art

The LS process itself can be divided in three temperature phases: preheating, building and cooling [6]. During preheating, several number of layers, which act as isolation layers, are applied in the building chamber of the LS system. The building phase consists of the three repeating steps material coating, energy input and consolidation. The building process starts with a material coating step, followed by the energy input. The cross section of the component is exposed via CO_2 laser and thus one layer of thermoplastic material is molten. Finally, the building platform is lowered by the thickness of one layer, which is between 80 and 150 μm and another process cycle is introduced. During the building process the building chamber is preheated to a temperature near the onset melting temperature but above the crystallization temperature [7]. A typical time for building one layer and thus repeating the three process steps is 40 s [6]. The temperature of the surrounding powder and the exposed components decreases as the building process progresses [8]. The injection process of the reactive liquid must be realized between the material coating and the energy input or between energy input and material consolidation processes. The boundary conditions a liquid material has to fulfill to be implemented in LS process are:

- high stability at building chamber temperature

- high curing rate for low UV interaction times

- high infiltration rate, which goes along with a low viscosity (i.e. a defined surface tension between the solid and the liquid)

- sufficient bonding between the powder is indispensable

- separation of the two components may not occur.

The implementation of UV reactive resins in LS process is challenging, due to the defined infiltration and curing behavior of the used material. Furthermore, the solidification of the two materials takes place at different times. The solidification of the resin takes place in each layer and whereas the solidification of the thermoplastic occurs after the building process. Therefore, both solidification process must be investigated in detail. Nevertheless the infiltration and the curing is of main interest in this investigation and the solidification will be analyzed in further research. The curing behavior of UV curing systems can be analyzed by UV-DSC measurements, which is for example demonstrated in [9].

Besides the curing of the resin, the infiltration of the liquid in the powder bed is of main importance, because it ensures a sufficient connection between two layers. The speed of infiltration and wetting of a powder layer by the used liquid does not just depend on the viscosity, but also on the surface tension σ and other characteristics. [10]

The absorption or rather interaction of droplets with porous media is studied both experimentally and numerically in different investigations. A short overview of relevant investigations is shown in [11]. Hua Tan [11] studied the pico liter ink impact with porous media with computational fluid dynamics (CFD), validation via high speed imaging and a set up like the one described in this paper. Nevertheless, the named study is focusing on Ink Jet process with aqueous inks and paper as substrate. The interaction of a droplet with a porous media can be divided into the stages initial spreading, absorption or infiltration and evaporation. The spreading kinetics is typically characterized by an equation of the following form [12]:

$$r(t) = Q \cdot t^n \tag{1}$$

with r the time-dependent droplet radius and the constants Q and n.

The infiltration or absorption can be calculated according to Denesuk et al.[13] by using the Washburn equation, assuming radial symmetry of the liquid and the porosity parameters and neglecting the finite size of the pore. The infiltrated volume V_P at time t can be calculated with the following equation:

$$V_p(t) = \frac{k}{2} \int_0^t \frac{r^2(t')}{\sqrt{t'}} dt' \tag{2}$$

$$k = \pi \cdot a_p \sqrt{\frac{\gamma_{LV} \cdot cos\theta \cdot R_{pore}}{2\eta}} \tag{3}$$

with R_{pore} the pore radius, a_p the area fraction of pores, γ_{LV} the surface tension of the liquid, θ the contact angle between the liquid and solid and η the viscosity.

Holman et al. studied the spreading and infiltration behavior of small droplets (approximately 60 µm) of aqueous polymer solutions on high green density porous beds [12]. The spreading and infiltration occurs in these investigations at the same time scale, precluding their treatment as a separate phenomenon [12].

The aim of this investigation is to analyze the curing behavior of UV, the curing acrylate systems and the interaction of these liquids with porous media like a powder bed. Furthermore, the boundary condition of curing and infiltration will be adapted to the temperatures in laser sintering process.

Materials and Methodology

Materials

Two different UV curing resins (Ultra Violet Light Curing DLP Hard and Ultra Violet Light Curing DLP Flexible) from the supplier PhotoCentric 3D were used as liquids. Within these investigations, the resins were abbreviated as UV-Hard and UV-Flex. The resins were chosen due to their low viscosity. At 25 °C the viscosity of the material UV DLP Hard is given as 230 cPs [16] and the one of the material UV DLP Flexible is 200 cPs [17]. Both systems are based on an acrylate material. On the raw material, the curing behavior was analyzed by UV-DSC measurements.

In laser sintering almost 90 % of the manufactured materials are based on polyamide [14]. Polyamide 12 is the plastic with the highest market share [15]. For the following investigations an unmodified virgin polyamide 12 (PA12) powder type PA 2200 from the supplier EOS GmbH, Germany is used as porous media.

The curing behavior of the pure resin and the infiltration of the resin into the powder bed of polyamide 12 were analyzed to determine whether these systems can be used in combined LS process. Therefore, the design of experiments shown in Table was conducted.

TABLE I.   DESIGN OF EXPERIMENTS

Curing behavior		
Material	*Time (s)*	*UV power (mW/cm²)*
UV DLP Hard	0.6, 1.2, 1.8, 2.4, 3.0, 3.6, 120	100, 200, 300
UV DLP Flexible	0.6, 1.2, 1.8, 120	100, 200, 300
Infiltration behavior		
Material	*Temperature (°C)*	
UV DLP Hard / PA12 powder	20 60	
UV DLP Flexible / PA12 powder	20 60	

Curing Behavior

The curing behavior was analyzed via UV-DSC measurements. A DSC type Q2000 from TA Instruments with an UV curing unit type OmniCure S2000 from Excelitas Technologies was used. An amount of

approximately 5 to 10 mg of material was heated to a temperature of 50 °C. After an isothermal phase, the sample was radiated with an UV lamp and the temperature development as well as the heat flow was detected. The interaction time varies between 0.6 and 120 seconds. A second one, with an interaction time of 2 minutes, follows the first radiation. After the second radiation, the specimen should be fully cured. A schematic diagram of the UV-DSC measurement is shown in Figure 2. The temperature and the enthalpy of the first and second UV curing step was analyzed, finally.
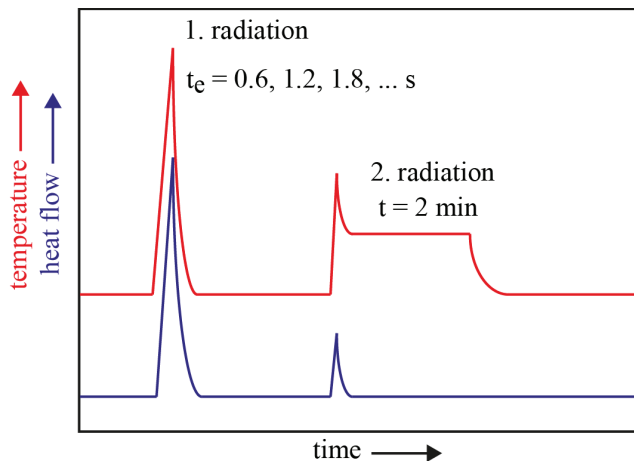

FIGURE 2: Schematic diagram of an UV-DSC measurement

Infiltration Behavior

For analyzing the infiltration behavior, a specific test set up for surface tension measurements from DataPhysics was used. The measurement scheme is visualized in Figure 3. This system is usually used to determine the surface tension of liquids solids. The measuring mode sessile drop was adapted to determine the development of the drop height dependent on time.

With a microliter syringe, a resin drop was applied on the powder bed surface. The drop is illuminated from one side by a light source and is observed by a CCD camera system on the other side. The infiltration of at least 10 drops was measured in order to calculate an arithmetic average. Furthermore, the minimum and maximum measurement values were determined. The development of the drop height and the contact angle was measured at 20 and 60 °C under nitrogen atmosphere.
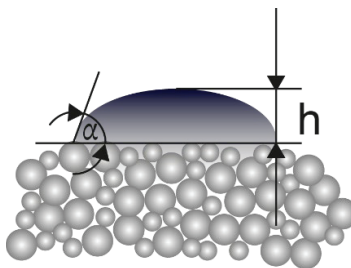

FIGURE 3: Scheme of the set up for analyzing the infiltration behavior of the resins into a powder bed

Results and Discussion

Curing Behavior

To analyze the curing behavior of the used resins UV DSC experiments were conducted. The UV radiation power and time was changed in order to analyze the needed energy input in hybrid LS process. A diagram of these UV DSC experiments is shown in Figure 4. The figure exemplifies a measurement curve of the UV DLP hard material for laser power of 100 mW/cm² and interaction time of 0.6 seconds. For the initial radiation, the resulting enthalpy and the maximum temperature were evaluated. The second radiation is used as post curing step and therefore the radiation time is long enough to ensure that the specimen is fully cured.
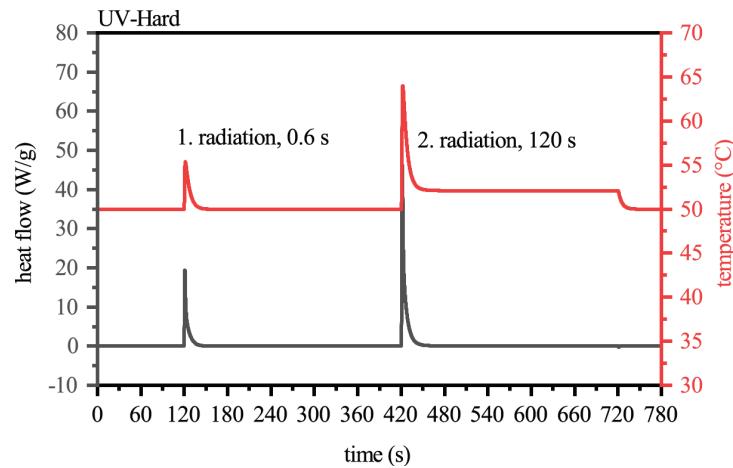
FIGURE 4: UV DSC measurements for the UV-Hard material for an interaction time of 0.6 seconds and power of 100 mW/cm²

Figure 5 shows the UV curing DSC two factorial experiment for the system UV-Flex. The intensity of the UV lamp was changed between 100, 200 and 300 mW/cm² and the radiation time between 0.6 and 120 seconds. The maximum temperature and the enthalpy, which is released during exothermic curing reaction, is evaluated for the first and second exposure. The time for the second radiation is 120 seconds to ensure a complete curing of the samples. Therefore, with the initial radiation the reaction itself is analyzed and with the post curing (i.e. the second radiation) the residual enthalpy is evaluated. With increasing time, the released energy during UV exposure rises up to approximately 300 J/g. For high radiation times the power of the UV curing step has no influence on the resulting enthalpy. However, rising the laser power from 0.6 to 1.2 seconds UV radiation time, the released enthalpy increases. The residual enthalpy, which is released during the post UV curing step decreases with increasing interaction time of the first radiation. Furthermore, the residual enthalpy is lower for higher UV powers, which is obvious due to equal total energy release of the fully cured system.
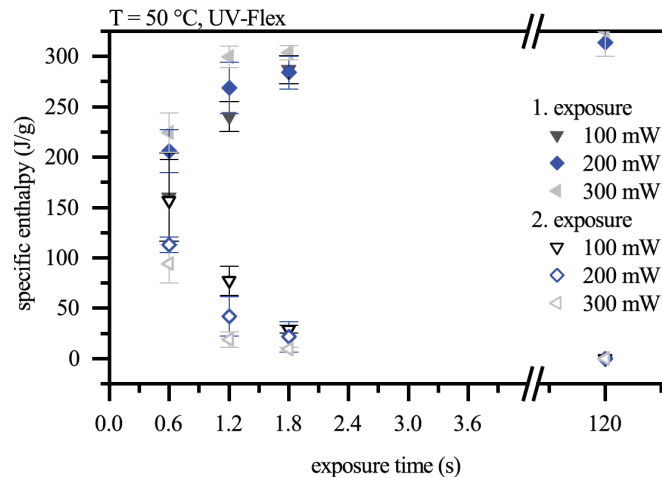

FIGURE 5: Enthalpy vs. UV power and radiation time for the first and second radiation of the UV-Flex material

The maximum temperatures during UV exposure for the material UV-Flex is represented in Figure 6. During first exposure, the maximum temperature of the material rises with increasing interaction time, which goes along with the curing progress and the released energy. Furthermore, the energy input has no significant influence on the resulting maximum temperature during UV irradiation. The temperature of the sample during the second heating is lower than for the first UV exposure with a value between 50 and 60 °C.
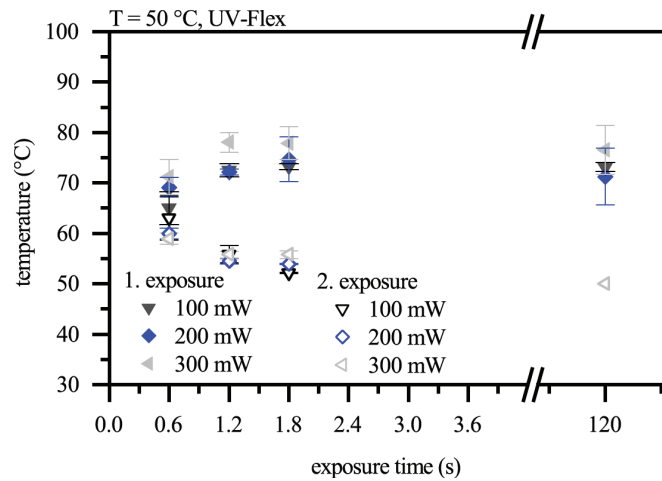
FIGURE 6: Maximum temperature in UV DSC vs. UV power and radiation time for the first and second radiation of the UV-Flex material

The residual enthalpy shown in Figure 5 is for the second radiation lower than for the first one. Thus, the temperature development due exothermic reaction is reduced. Furthermore, the maximum temperature is independent from the energy input and it is decreasing slightly with increasing exposure time. For long impact time and thus a high degree of cure or polymerization, nearly no increase of temperature can be detected. Compared to the basal temperature of 50 °C the specimen's temperature is not heightened for long radiations times during the second heating. For further investigations the basic temperature will be increased in order to analyze whether there is an influence of the surrounding temperature on the cross linking process. The aim would be to simulate the process conditions and therefore temperature up to 150 °C (assumed interaction temperature of the resin with a PA12 powder, which was manufactured at a building chamber temperature of 167 °C) will be investigated.

Figure 7 and Figure 8 shows the enthalpy and the maximum temperature of the UV DSC measurements for the first and second irradiation for the UV-Hard material. The enthalpy is rising with increasing UV radiation time and with increasing UV power during the first heating. This trend could also be observed for the material UV-Flex. The absolute level of released energy is higher for the material UV-Flex compared to UV-Hard. The evaluation of the second radiation shows a reduction of the enthalpy with increasing time of the first UV exposure. For high impact times the residual enthalpy tends to zero. Thus, the whole reaction takes place during the first exposure. To adapt this behavior to the hybrid laser sintering process it is important to ensure that a residual amount of material can react during the second UV irradiation to get a sufficient connection between two applied layers of UV resin. Therefore, short exposure time are favored for the final hybrid process.
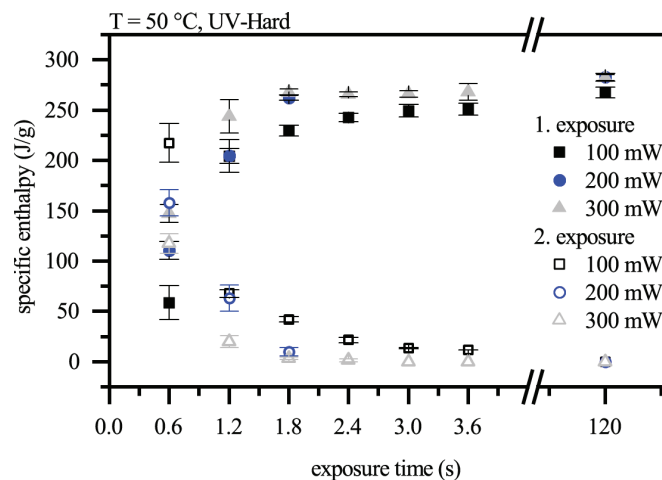
The resulting maximum temperature during the first and second UV irradiation is represented in Figure 8. With rising impact time, the temperature during first irradiation increases from approximately 55 °C (100 mW/cm²) to 65 °C (100 mW/cm²). Furthermore, the temperature seems to be dependent on energy input. For higher UV power the maximum temperature rises. The post curing after the initial UV curing steps shows an increase of temperature for higher radiation times. Due to a lower value for exothermic reaction, the temperature rise is reduced and for the specimen with a radiation time of 1.8 seconds (first radiation) no significant temperature increase compared to the basal tempering could be detected. In comparison to the material UV-Flex the temperature value of the resins UV-Hard is lower.
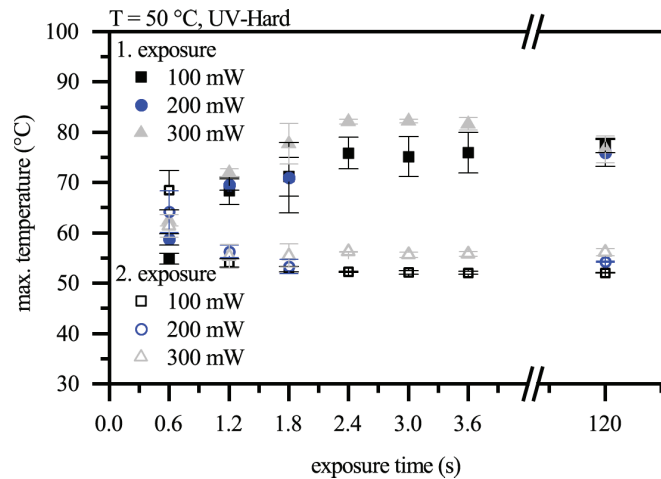

FIGURE 8: Maximum temperature in UV DSC vs. UV power and radiation time for the first and second radiation of the UV-Hard material

Infiltration Behavior

For combined LS process with reactive resins the curing and the infiltration behavior plays a major role. Therefore, the infiltration was analyzed with a test set up, which was adapted from surface tension measurements. Figure 9 shows the development of droplet height for two different surrounding temperatures for the material UV-Flex. As substrate a PA12 powder was used. The median curve was calculated on basis of at least 10 droplets and the black and red lines show the minimum and maximum values of the measurements. With increasing temperature, the infiltration of the liquid in the powder bed is accelerated.
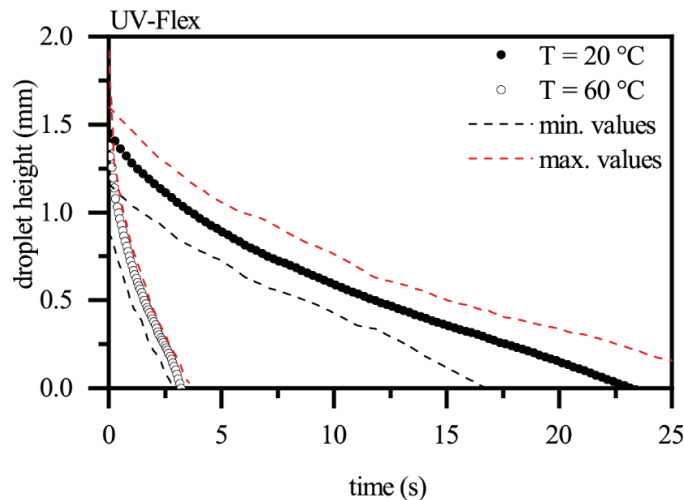

FIGURE 9: Droplet height vs. interaction time and temperature for the UV-Flex material

For a temperature of 20 °C the infiltration takes approximately 23 seconds, whereas for 60 °C the absorption is finished after approximately 2 seconds. Measurements for higher temperatures near building chamber temperature cannot be realized with this test set up, due to short infiltration times. Therefore, the set up

will be equipped with a high speed camera in the future. For average layer time in LS of approximately 40 seconds the infiltration process is fast enough to avoid a slowdown of the whole production process. The initial droplet height is independent from the surrounding temperature.

The droplet development for the material UV-Hard is shown in Figure 10. As substrate material, a polyamide 12 powder with a bulk density of 0.43 g/cm³ was used. The infiltration for such absorption process shows an equal trend than the one for the UV-Flex material (Figure 9). The infiltration depends on the temperature, which can be traced back to the reduction of viscosity with increasing temperature. The initial droplet height shows a similar level for both analyzed materials.

Link in curing experiments in further investigations the temperature of the powder bed will be increased to simulate the laser sintering process. In laser sintering of PA12 the building chamber is heated up to 167 °C and thus assumed interaction temperatures lay between 140 and 160 °C when the droplets have a temperature of 50 or 60 °C. Unfortunately, with the shown set up the infiltration for higher temperatures cannot be traced. Therefore the set up is equipped with a high speed camera in the future.
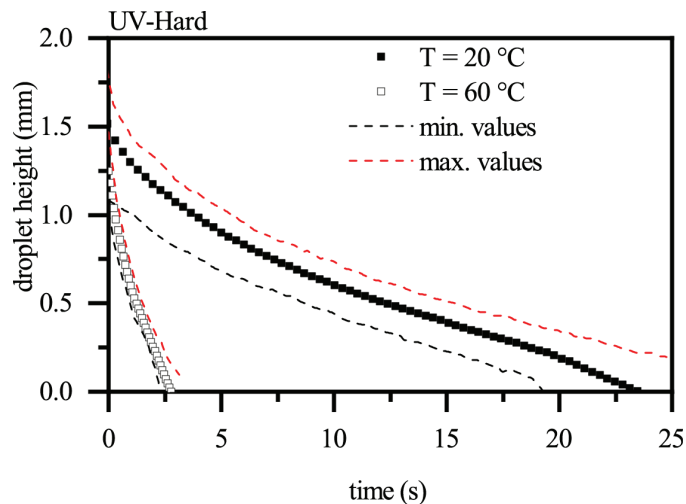

FIGURE 10: Droplet height vs. interaction time and temperature for the UV-Hard material

Summary and Outlook

In this research work, a new process route to produce multi-materials parts in laser sintering (LS) is introduced. The process itself is adapted from powder binder techniques combined with laser sintering of polymers. Therefore, reactive resins were implemented in these LS processes. Besides the melting of the thermoplastic materials, a resin is cured via UV light. The curing behavior of UV acrylate based resins and the infiltrations performance of the liquid in combination with a powder bed were analyzed.

The curing of the materials was analyzed via UV DSC measurements and under variation of impact time and UV power. With increasing time and power the exothermic reaction progresses. Furthermore, the temperature of the specimen rises due to higher exothermic reaction. The specimens were exposed to the UV light source a second time in order to analyze the residual enthalpy. For long initial curing times no significant energy release could be detected, which indicates a complete curing during the first UV light exposure. This time and power combination are not favored due to the need of bonding between two layers, which goes along with a residual reaction energy.

Besides the curing, the infiltration is analyzed with a specific test set up, which is adapted from surface tension measurement. The infiltration time for both resins into a PA12 powder bed take less than 25 seconds at room temperature. For an expected layer time of 40 seconds, an infiltration speed lower than 25 seconds is favored. With increasing temperature, the infiltration of the dispended droplet is even faster. Thus, both materials will infiltrate the powder bed in an adequate time. Nevertheless, the parallel running of the curing and infiltration steps should be analyzed in further studies. Therefore, the test set up will be modified with an UV light source.

Furthermore, the curing and the infiltration will be analyzed at higher temperatures, which are nearer at the laser sintering of thermoplastic materials in further investigations. For PA12 powder the building chamber temperature is for example between 165 and 172 °C. The droplets will be stored in a tempered syringe at a temperature between 50 and 60 °C. Thus, a temperature between 140 and 160 °C is assumed as interaction temperature. Therefore, both test set ups will bed adapted in the future to analyze the curing and infiltration behavior process adapted.

Acknowledgement

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