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Reviewed Paper

CURING BEHAVIOR OF THERMOSETS FOR THE USE IN A COMBINED SELECTIVE LASER SINTERING PROCESS OF POLYMERS

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Abstract

Selective laser sintering (SLS) of polymers is an additive manufacturing process, which enables the production of functional technical components. Unfortunately, the SLS process is restricted regarding the materials that can be processed and thus resulting component properties are limited.

The investigations in this study illustrates a totally new additive manufacturing process which combines reactive liquids like thermoset resins and thermoplastics to generates multi material SLS parts. To introduce thermoset resins into the regular SLS process, the time-temperature-dependent curing behavior of the thermoset and the infiltration behavior has to be understood in order to assess the process behavior. The curing behavior was analyzed by rotational viscosimeter. Furthermore, the fundamental infiltration behavior was analyzed with micro dosing infiltration experiments. Finally, a thermoset resin in combination with a dosing system was choosen for integration in a laser sintering system.

Introduction

Additive manufacturing technologies, like selective laser sintering (SLS) of thermoplastic powders, generate components directly from a CAD dataset without needing a form or a mold. Thus, the layerwise process of selective laser sintering allows the generation of individualized complex serial parts. Contrary to conventional manufacturing techniques like injection molding, which are optimized for high volume production and low unit costs, the costs for additive manufactured parts are almost independent from the degree of complexity and the quantity [1]. The advantages of additive technologies are favored for products with high customization, a high level of complexity and small lot sizes, which is known as “mass customization” [2].

Although there are efforts to develop new materials for SLS [3-7], the availability of polymers that can be processed in SLS is still very limited compared to conventional manufacturing methods like injection molding. Beside polyamide 12 and polyamide 11, filled systems and a few other thermoplastic materials like polypropylene and thermoplastic elastomers are available at the market [8]. The reason for the slow development of new polymers powders for SLS is the small market value. The market for SLS powders is with 900 tons/year compared to 260 million tons of worldwide plastic used very small [8]. Nevertheless, there is a huge customer demand for new applications of additive technologies. The limited component characteristics, which can be reached with the available materials, hinders the use of SLS for specific applications. The local adjustment of certain properties and thus the generation of multi-material parts could lead to significantly higher rates of usage of SLS manufactured parts, because the achieved properties could cover more specifications. Therefore, in this paper a new unique additive manufacturing process, which overcome the bridge to create new properties in SLS, will be introduced. The hybrid process between powder

binder techniques and SLS integrates reactive liquids in the SLS process, as shown in Figure 1. These fluid materials are planned to be injected into a conventional SLS powder bed through a micro valve system and the reaction of the liquid is initiated via IR or UV radiation. Beside the reactive liquid, the thermoplastic powder can be processed in SLS like usually. Thus, multi material parts consisting of a reactive system like an epoxy resin and a thermoplastic material can be generated in one process.

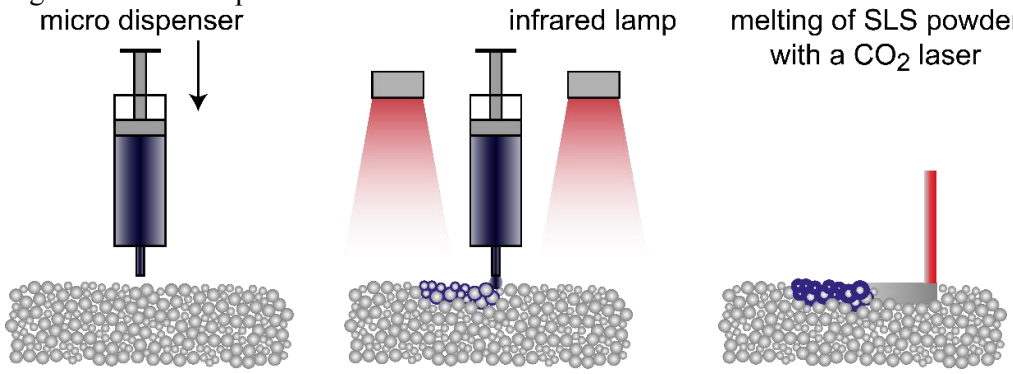

Figure 1: Schematic visualization of the hybrid SLS process with reactive liquids

State of the art

The SLS process itself can be divided in three temperature phases: preheating-, building- and cooling phase [9]. The building process consist of the three steps: material coating, energy input and consolidation. Firstly, a layer of powder is applied in the building chamber. The layer thickness of the coated layer is usually between 80 and 150 µm. Secondly the cross section of the component is exposed by a CO_2 laser and the materials starts to melt selectively. Finally, the building platform is lowered by the thickness of one layer and the three process steps will be repeated. During building process the building chamber is preheated to a temperature near the onset melting temperature but above the crystallization temperature [10]. A typical time for building one layer and thus repeating the three process steps is 40 s [9]. The temperature of surrounding powder and the exposed components decrease the farther away the point of measurement is from the powder surface [11]. The implementation of the reactive liquid in the hybrid process must be done after material coating and before or parallel to the energy input via CO2 laser. The boundary conditions a liquid material has to fulfill to be implemented in SLS process are:

- high stability at building chamber temperature
- specific curing behavior under the temperature occurring in SLS
- high infiltration rate, which goes along with a low viscosity a defined surface tension between the solid and the liquid
- separation of the two components may not occur.

Thus introducing a material that reacts during SLS process presents a specific challenge. In order to develop thermosets for SLS process, the curing under a specific temperature profile, which is determined by the SLS process itself, must be monitored precisely. The thermal household during SLS will be influenced for example by the energy input (laser power, scan speed, …), the number of exposed components, the chamber and feeder temperature. Besides the curing of the resin the infiltration of the liquid in the powder bed is of main importance, due to ensure 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, as exemplarily depicted in Figure 2. [12]

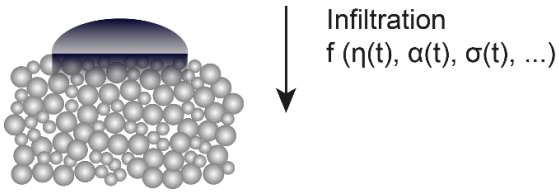

Figure 2: Fluid powder bed interaction

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 [13]. Hua Tan [13] studied the pL impact with porous media with computational fluid dynamics (CFD) and validation via high speed imaging and uses a similar set up like 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 divided into the stages initial spreading, absorption or infiltration and evaporation. The spreading kinetics is typically characterized by an equation of the following form [14]:

$$r(t) = Q \cdot t^n \qquad (1)$$

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.[15] by using the Washburn equation and 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 can be calculated with the following equation:

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

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

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 [14]. The spreading and infiltration occurs in this investigations at the same time scale, precluding their treatment as separate phenomena [14].

The aim of this investigation is to analyze spreading and infiltration behavior with a specific test set up and determine whether spreading and infiltration can be separated. Furthermore, the influence of the pore size or rather bulk density as well as the surface tension of the used liquid on the infiltrations behavior is main interest.

Methodology

Material / powder

For the following investigations an unmodified polyether block polyamide powder (PEBA) type PrimePart ST from the supplier EOS GmbH, Germany is used. PEBA is a thermoplastic elastomer consisting of polyamide and polyether backbone blocks. Two different aging states of the powder, virgin and used powder was used, in order to analyze the infiltration

behavior dependent on the bulk density of the material. Figure 3 shows a scanning electron microscopy image of the PEBA powder.

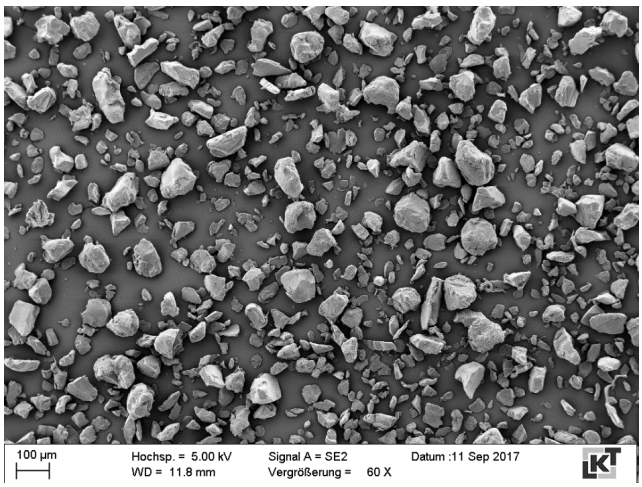

Figure 3: Scanning electron microscopy image of PEBA powder

A DSC diagram of the used PEBA is shown in Figure 4. On basis of the DSC analysis, the building chamber temperature should be chosen between 125 and 137 °C for this material. Furthermore, material properties of the used resins like surface tension and viscosity are of main interest at a temperature interval near building chamber temperature. Due to reduction of temperature during coating machismo of up to 30 K. The relevant temperature range is between 100 and 130 °C.

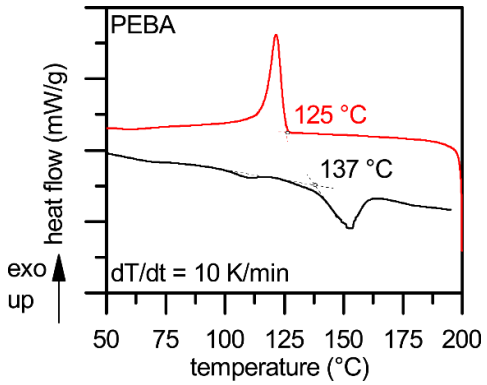

Figure 4: DSC diagram of the used PEBA powder

Material / resins

As reactive liquid two epoxy resins Araldite GY 764 and Araldite GY 793 purchased from Huntsman Advanced Materials, Switzerland was used. Araldite GY 764 is based on bisphenol A, whereas GY 793 is based on bisphenol A/F. The used curing agent, Hardener XB 3473, was also purchased from Huntsman Advanced Materials. The used mixing ratios were 100:23 parts per weight for GY 764 and 100:22 parts per weight for GY 793. The epoxy resins were selected because of their low viscosity and their high reaction temperatures, which deem them compatible with the sought processing through a micro valve in the hot building chamber. GY 764 possesses a viscosity of 350 - 550 mPas, GY 793 650 - 750 mPas and the Hardener XB 3473 80 - 125 mPas [16]. For the further investigations, the mixtures of Araldite and Hardener are abbreviated with the pure resin names Araldite GY 764 and Araldite GY 793.

Characterization of material properties

The **surface tension** of the used resins was analyzed with the pendant drop method and the surface tension measurement set up from the company DataPhysics. At least 10 drops were dosed and evaluated according their dimensions. The Laplace-Young equation was used to calculate the surface tension of the liquid.

The **viscosity** of the resins was determined with a rotational viscometer type Discovery HR-2 from TA Instruments. As measurement geometry, a plate-plate set up was used. The frequency was set to 0.1 Hertz and the normal force was 10 Pascal. The uncured mixture was applied between the two plates at a starting temperature of 25 °C and the specimen was heated with a heating rate of 2 K/min up to 200 °C. Finally, the complex viscosity was analyzed dependent on the temperature.

Beside the influence of the temperature, the influence of the **bulk density** on the infiltration behavior will be investigated. Therefore, the bulk density was analyzed according to DIN EN ISO 60 [17]. The bulk density is defined as the mass of the polymer particles divided by the total volume they occupy. For the analysis a bulk density tester from Emmeran Karg Industrietechnik type ADP is used. The average was calculated out of at least five measurements.

Infiltration behavior

For combined laser sintering process the infiltration behavior of the reactive liquid in the powder bed is of main interest. Therefore, the infiltration behavior was analyzed with a specific test set up, which is schematically illustrated in Figure 5. For the measurements, a basic set up from the company DataPhysics was used. This system is usually used to determine the surface tension of liquids with the pendant drop method and the surface tension of solid with for the sessile drop method. The measuring mode sessile drop was adapted to determine the development of the drop height dependent on time. Thus, the infiltration of the liquid in the powder bed can be evaluated. Furthermore, the angle between the powder bed surface and the liquid was analyzed.

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. The development of the drop height and the contact angle was measured at 20, 40 and 60 °C under nitrogen atmosphere. Figure 4 shows, that the temperature range between 100 and 130 °C is of main interest due to building chamber temperature. Nevertheless, the infiltration at these temperature takes less than 1 second and is hardly analyzable. Table 1 represents the detailed design of experiments.

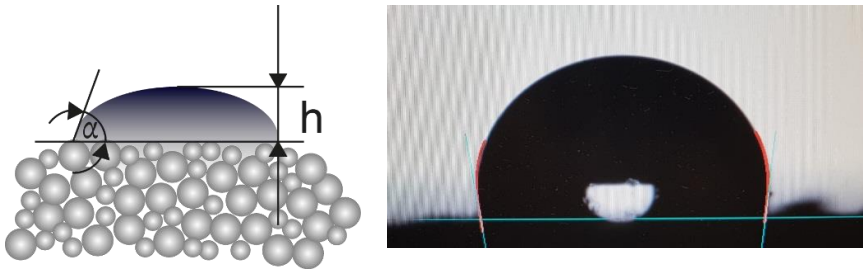

Figure 5: Scheme of the measurement of the infiltration behavior of the resin in a powder bed

Table 1. Design of Experiments

Resin	Bulk density powder (g/cm³)	Temperature (°C)
Araldite GY 764	0.39	20
		40
		60
	0.36	20
		40
		60
Araldite GY 793	0.39	20
		40
		60
	0.36	20
		40
		60

Results and discussion

First, the bulk density of the used substrate materials, a thermoplastic elastomer with a volumetric median particle size of 77 µm, was analyzed. As substrate material virgin powder and powder that has passed through one processing cycle was chosen. The virgin powder shows an average bulk density of 0.39 g/cm³, Figure 6. With increasing number of processing cycles, the bulk density decreases to a value of 0.36 g/cm³, Figure 6. The packing density of the bulk material can be calculated by dividing the bulk density and the density of the solid material. Thus, the packing density of the used material is 35 % and 33 % for a solid material density of 1.1 g/cm³.

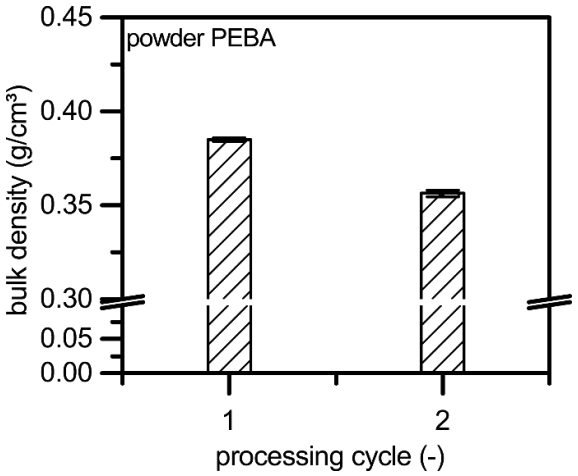

Figure 6: Bulk density of the substrate powder

Beside the influence of the porosity of the substrate material, the influence of the used liquid resin and thus the surface tension and it's viscosity on the infiltration behavior was determined. Therefore, the surface tension of the resins Araldite GY 764 and Araldite GY 793 was measured via pendant drop method and calculated according the Laplace-Young equation, Figure 7. The resin with the trade name Araldite GY 764 shows with a value of 37 Nm/m a higher surface tension than the resin with the trade name Araldite GY 793. Nevertheless, the surface tension cannot be linked directly to the infiltration speed due the influence of viscosity and contact angle on the infiltrated volume expressed in equation 3.

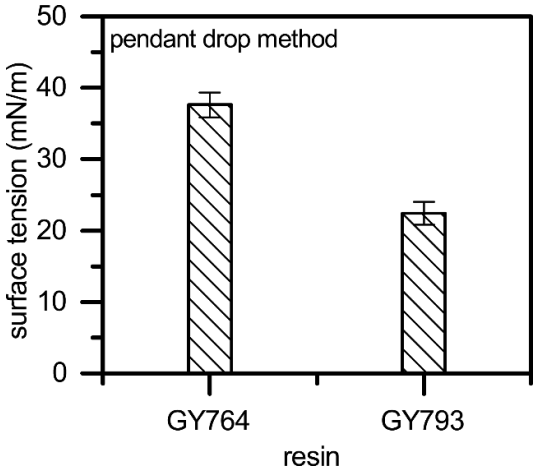

Figure 7: Surface tension of the used resins

The viscosity and surface tension are determining the absorption behavior of liquids in porous structures according to equation 2. For this reason, the temperature-dependent viscosity of the resins was analyzed. Figure 8 shows the complex viscosity in dependency of temperature for a heating rate of 2 K/min. With increasing temperature, the viscosity shows a first decrease, which can be linked to the higher mobility of chain segments with rising temperature. For higher temperatures, the crosslinking or rather curing process takes place and the viscosity rises. The minimum viscosity is reached in a temperature interval between 100 and 120 °C for both resin and hardener mixtures. The curing reaction starts for a heating rate of 2 K/min at a temperature of 100 °C. This value depends is time and temperature and thus the heating rate plays a major role. Comparing the two resins, the curing behaves almost equal. The system with the trademark Araldite GY793 shows a slight delay in the viscosity increase.

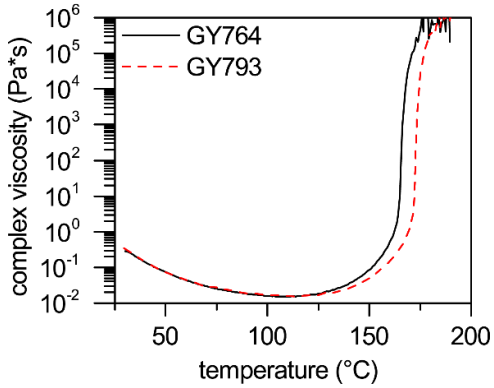

Figure 8: Viscosity of the used resins

The infiltration behavior of the used resins is shown in Figure 9. Therefore, the droplet height is plotted against the interaction time. The broken lines represents the minimum of maximum value of the mearsurements, which was calculated on basis of at least 10 droplets. For a temperature of 20 °C a total infiltration of the droplet into the substrate cannot be detected for both resins. The initial droplet height is higher for the resin with the trademark Araldite GY 764. This fact in combination with equal contact angles in Figure 10 lead to the assumption, that the volume of one drop of the resin GY 764 is higher than the volume of the droplet GY793. The droplet height decrease during the first 5 to 10 seconds faster than during the remaining time. With increasing temperature, the infiltration time decreased dramatically for both systems. For a temperature of 60 °C the total infiltration takes only approximately 2 seconds. This

acceleration of the infiltration process goes along with the reduced viscosity and thus the higher volume of liquid material, which can infiltrated the porous structure according to equation 2. For layer times of approximately 40 seconds in selective laser sintering an infiltration time of only 2 seconds is favored because the infiltration itself must not enlarge the processing time.

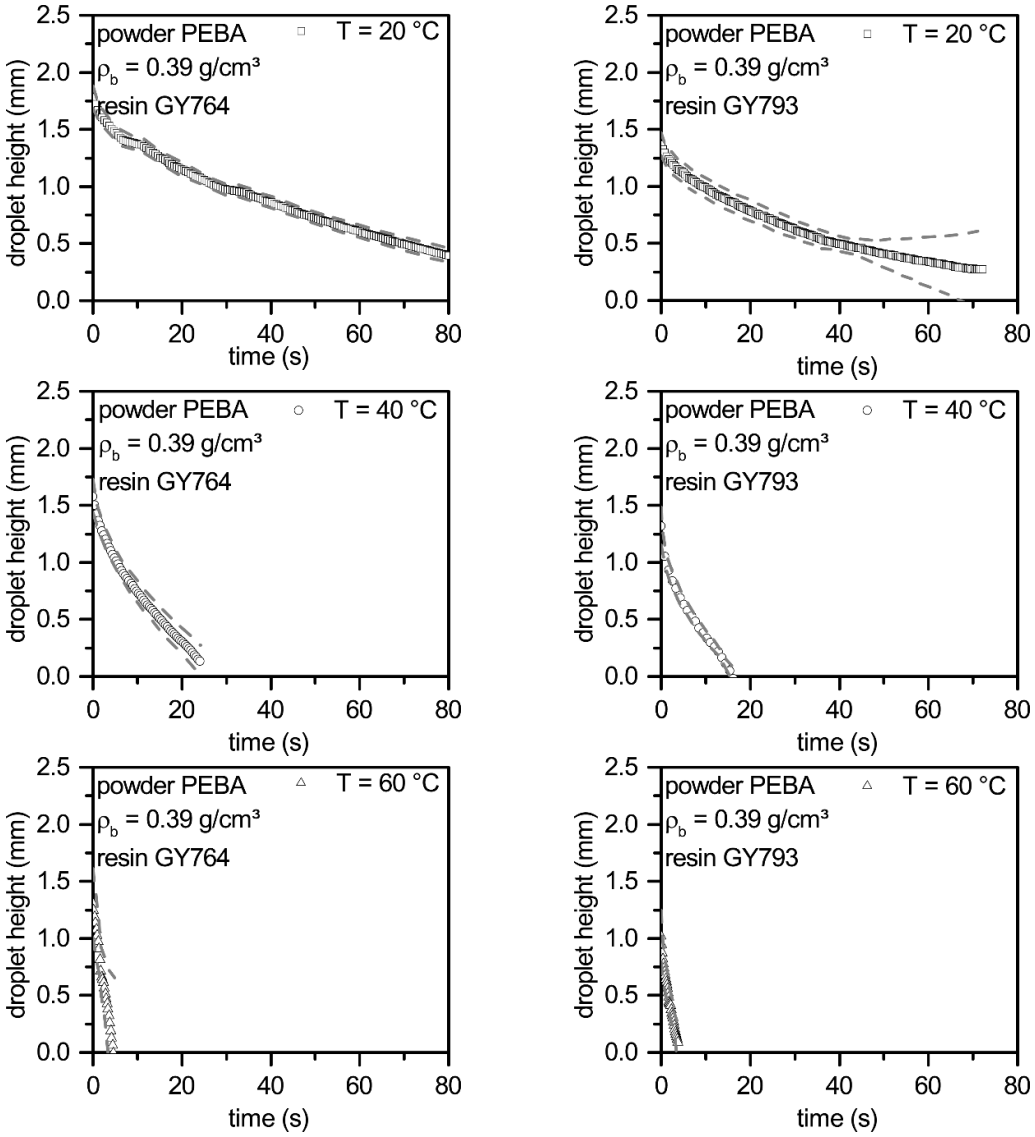

Figure 9: Droplet height dependent on time for different temperatures and resins, bulk density 0.39 g/cm³

The infiltration behavior of the resins in a substrate with a higher porosity compared to Figure 9 is represented in Figure 10. The bulk density of the substrate changes from 0.39 g/cm³ to 0.36 g/cm³. This increase of porosity lead to an increase of infiltration speed, Figure 8 and Figure 9. At room temperature, the resin with the trademark Araldite GY764 infiltrated the porous structure in less than 60 second (Figure 10), whereas for a substrate bulk density of 0.39 g/cm³ after 80 seconds there is still a droplet height of 0.5 mm measurable. For the substrate with the bulk density of 0.36 g/cm³ the deviation between the minimum and maximum values are larger than for the powder with a bulk density of 0.39 g/cm³. This may be a result of inhomogeneous packing and thus an irregular infiltration. The comparison of the two resins demonstrates a slightly faster infiltration in the case of Araldite GY 793. As shown before the infiltration speed increases with rising temperature due to the reduced viscosity of the resins.

For temperatures above 60 °C the absorption of the liquid is even faster and the contact angle as well as the droplet height cannot be detected any more.

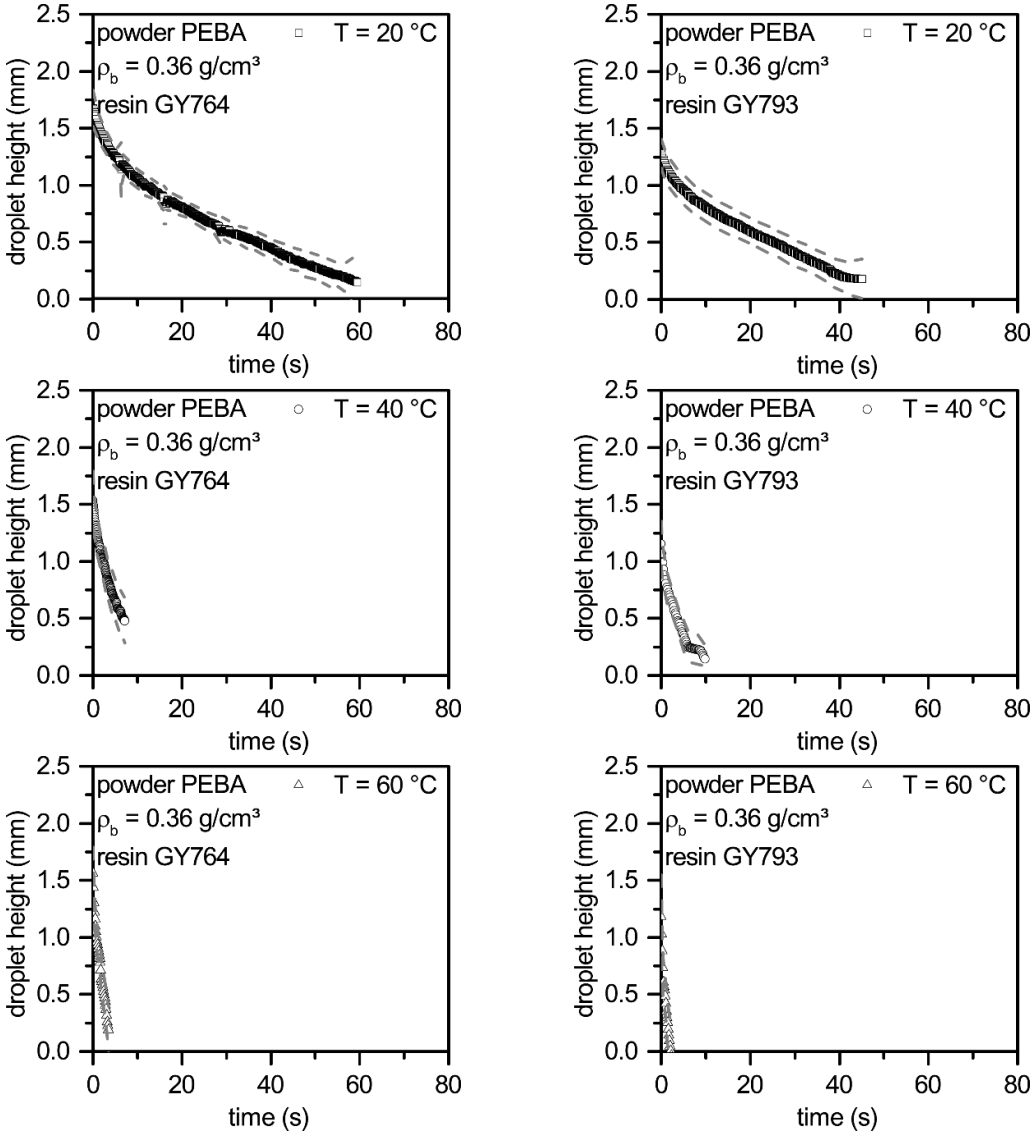

Figure 10: Droplet height dependent on time for different temperatures and resins, powder: PEBA bulk density 0.36 g/cm³

The contact angle between the liquid resin and the bulk material is illustrated in Figure 11 for different resins, bulk densities and temperatures. Compared to the droplet height the initial contact angle is at the same level for both resins. The contact angle decreases faster with increasing temperature for both substrates and resins. This can be traced back to the reduced viscosity in Figure 8. Furthermore, the contact angle shows almost the same tendencies like droplet height. For a temperature of 60° the contact angle tend to zero after less than 5 seconds and thus the process speed is not influenced dramatically in selective laser sintering.

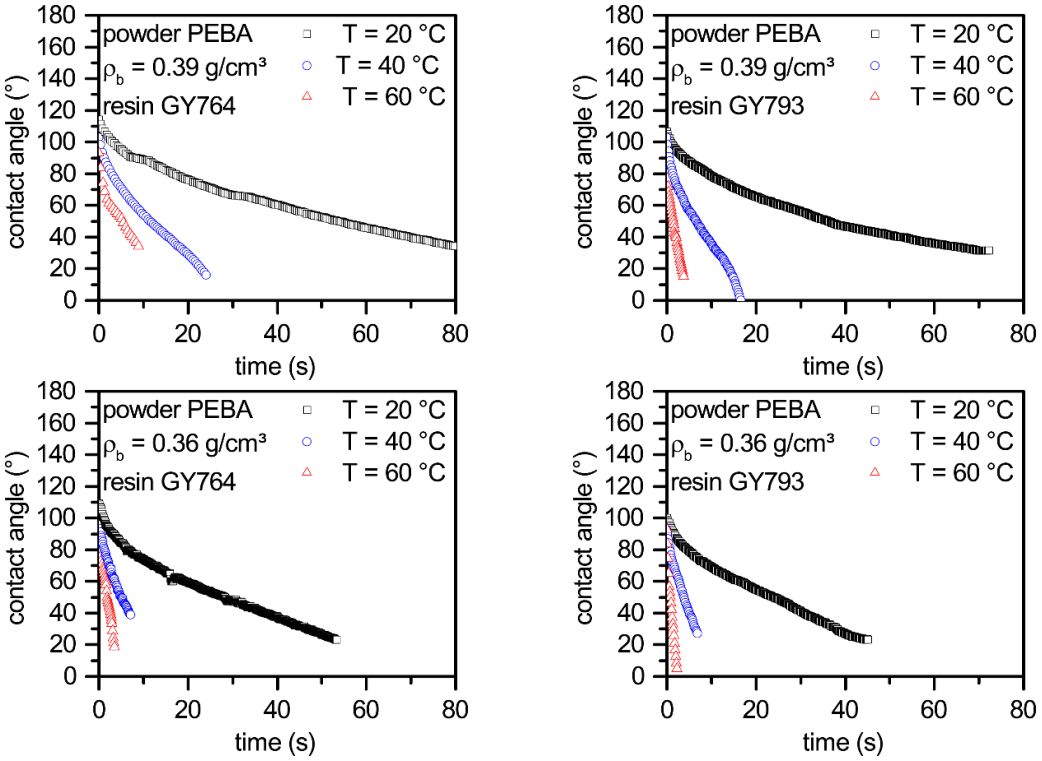

Figure 11: Contact angle dependent on time for different temperatures, resins and bulk densities

Figure 12 shows microscopy images of a cross section of a sample of PEBA with the resin GY 764. The samples were prepared in a selective laser sintering system type DTM Sinterstation 2000. The building chamber temperature was 130 °C (see DSC diagram Figure 4) and the liquid droplet and the powder material was exposed with a CO2 laser. The images show, that the infiltration depth of the liquid is higher than the laser material interaction zone, which is visible as white areas. The used resin is absorbed into a thickness of approximately 1,000 µm. In regions far away from the surface the PEBA is not molten and the particles glue together due to the surrounding epoxy material. Nevertheless, these experiments show a principle feasibility of the represented hybrid process.

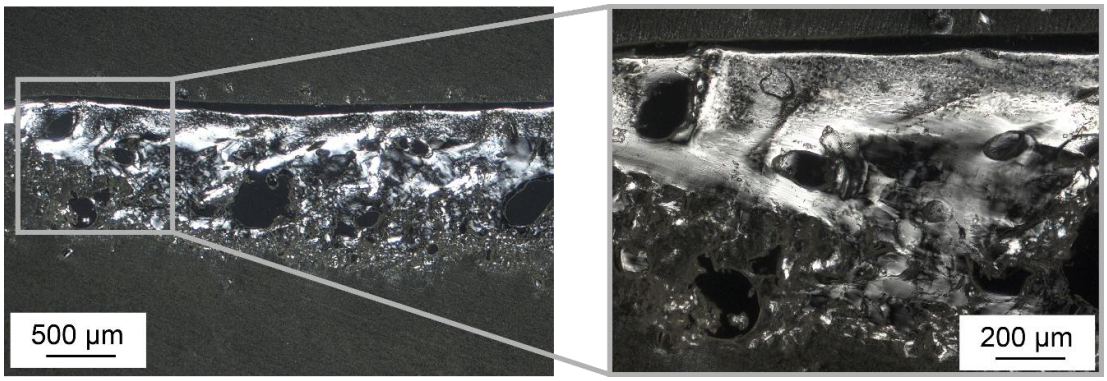

Figure 12: Microscopy image of PEBA sample, which was infiltrated with a droplet of the resin GY 764

Conclusions

This paper introduces a new hybrid additive manufacturing techniques, which will overcome the hurdle to manufacture multi material part in one additive process. With selective laser sintering of plastic only one material can be processed up to now. The implementation of reactive liquids, like epoxy resins, in the laser sintering process allow the generation of multi material parts. Therefore, the curing and infiltration behavior of the used resins has to be understood.

The interaction of the resin with the porous powder bed is investigated with new test set up. The development of droplet height and the angle between the powder bed and the liquid were determined and linked to the infiltration behavior. For both analyzed epoxy resins Araldite 764 and Araldite 793 the Hardener XB 3473 was used. With increasing temperature the infiltrations process is accelerated for both resins. This goes along with the reduced viscosity with increased temperature. At 20 °C the resin does not infiltrate the powder bed in total. For the highest analyzed temperature of 60 °C the infiltration takes less than 2 seconds. This means for layer times in selective laser sintering of 40 seconds and processing temperature of the powder bed surface of 120 °C the infiltration process will not determine the processing time. Thus, the analyzed systems can be used in combined laser sintering process. Nevertheless, the infiltration depth and the parallel curing must be analyzed in further investigations.

Acknowledgements

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