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DEVELOPMENT OF AN EXPERIMENTAL LASER SINTERING MACHINE TO PROCESS NEW MATERIALS LIKE NYLON 6

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Abstract

Selective Laser Sintering (SLS) is an Additive Manufacturing technology which allows the production of functional polymer parts. Conventionally, Nylon 12 (PA 12), Polyamide 11 (PA 11), glass- or aluminum filled materials are used. Those materials do not always meet the requirements for direct production of serial parts by laser sintering. For the so called “Direct Manufacturing” of high quality, functional parts, the laser sintering process needs to be further developed and the choice of materials and needs to be expanded.
During this research, a laser sintering machine for material qualification has been built up. The advantages are an optimized software solution, an innovative optical system with an adjustable laserspot, an alternative powder coating system and an improved temperature control.
The functionality of the test equipment is proved with the standard material PA2200 and the new laser-sintering-material, Polyamide 6X (PA6X) is investigated. The required process parameters for processing PA6X are derived and the mechanical properties are determined by tensile tests.

Introduction

Selective laser sintering (SLS) allows the direct production of functional plastic components. A digital 3D model is cut into layers and built up by adding material. For this purpose, a thin layer of the plastic powder is applied and preheated and the powder bed surface is heated up to a temperature just below the melting point. Subsequently, a CO_2 laser selectively exposures the layer-specific cross-section of the part. The plastic powder is locally melted by the laser. This iterative process of powder-coating, pre-heating and laser exposure is repeated until the part is finished. After the construction process, the additively manufactured parts are surrounded by unprocessed powder and the parts, that are not yet dimensionally stable, cool down slowly. After this cooling phase the parts can be removed from the so-called powder cake. The unmolten support powder can be sieved and reused for the next build-up process. State of the art is processing of Polyamide 12 (PA12), Polyamide 11 (PA11) and aluminum- or glass-filled compounds. The use of the laser sintering process for direct production requires the qualification of engineering plastics that meet the requirements of the end products. The material PA 6 is for example known from injection molding. With the aim of substitution of injection molding by laser sintering, PA 6 needs to be qualified for laser-sintering. The current laser sintering-machines of leading manufacturers, like EOS and 3D-Systems, do not always meet the requirements to process technologically significant materials such as PA 6, because of limited processing temperature and unprecise temperature control. [SCH15]

With the aim of processing new materials by SLS, an experimental SLS machine for material development was engineered and the new powder material Vestosint Z2657 PA6X was processed. The paper is structured as follows: First, the state of the art is described and the need for research is clarified. After that the developed laser sintering machine, PROTIQ HT LS, is presented. Using the known material PA2200, the functionality of the high performance SLS machine is proven. Finally, the new powder material PA6X is tested, process-parameters are identified and mechanical properties are determined with tensile tests.

State of the Art

The market-leading machine manufacturers, EOS and 3D systems, use different systems for powder coating. The powder is either applied with a blade, a cassette with two blades or a counter-rotating roller [BD89][WMP10]. Conventionally used powders are optimized for selective laser sintering and characterized by a good flow behavior. These materials can be applied properly with the existing coating systems and offer the basis for the following process steps: pre-heating and exposure. For material development, the production of small powder quantities is important. For this purpose, polymer granules can be crushed to powder by cryogenic grinding [GHT10]. However, powder application tests in conventional laser sintering systems have shown that cryogenically pulverized powder materials cannot always be applied uniformly, smoothly and dense. Bourrel presents the idea of an alternative coating solution with a combination of a blade and a roller, to realize a high powder density in the SLS process. First the powder is applied by a blade and as a second step compacted by a rotating roller [BW14]. None of the aforementioned solutions alow processing of grinded powders with poor free-flowing properties.

After powder coating, the powder surface is heated. Radiant heaters warm up the powder to a temperature just below the melting temperature. Subsequent to the application of the new powder layer, a CO_2 laser selectively fuses the new powder coating with the former layers that are still molten. The molten phase is maintained by continuous surface heating while the isothermal but non-exposed powder is still solid. If the adjusted preheating temperature is too high, the entire powder cakes. If the preheating temperature is too low, the melt solidifies and shrinkage occurs. Shrinkage results in part deformation and the so-called “curling” can lead to coating errors and process break-off. The permissible temperature range between sintering of the powder cake and the curling is material-specific. A precise temperature control is essential for processing sensitive materials [GEb07] [Sch15]. Wegner measured the temperature distribution on the powder bed surface of conventional laser sintering machines. As an example the offset-temperature of an EOS P100 is 8.7 ° C [WW13]. The inconsistent temperature distribution on the powder bed surface leads to position-dependant part properties [Dre16]. The maximum adjustable preheating temperature in the machine series EOS P3 and P1 is < 200 ° C. For this reason processing of materials like PA6, which has a melting point over 200°C, is not possible without machine modifications. Besides the uniform preheating, the total quantity of heat, consisting of preheating warmth and laser exposure warmth, is process-relevant. The laser energy input can be estimated by the laser energy density [MH08]:

$$E = \frac{P}{v * h} \qquad \text{and} \qquad EV = \frac{P}{v * h * t}$$

The energy density (E) in J / mm² is typically defined as a function of the laser power (P), the laser spot speed (v) and the laser path spacing (h). Since the precise melt pool geometry and penetration depth is typically not known, the layer thickness (t) is used to calculate the volume energy density (EV) in J / mm³. In order to identify the material-specific energy density by sintering tests, a free choice of the mentioned parameters is required. The SLS-systems, that are currently available on the market, do not offer the possibility to adjust all process relevant parameters.

Conventionally for laser-exposure an optical laser system with a fixed spot diameter is used. With the aim of direct production by SLS, the speed of the SLS-process gains importance. In order to decrease exposure times, the scanning speed has been steadily increased: The first machine generation, DTM Sinterstation 2000 from the year 1992, worked with a maximum scanning speed of 1.3 m / s and the current P396 from EOS exposures with a scanning speed of 6 m / s [DTM93] [EOS16]. Proportional to the scanning speed, the laser power was increased in order to ensure the material-specific, required energy input. Due to high laser powers, a Gaussian energy density distribution over the laser beam diameter and a low heat conduction in the plastic powder, energy peaks on the powder surface result. As a result of this energy concentration, the material can be overheated locally and degrades.
Drexler detected, that material properties do not only depend on the laser energy density, but also on the interaction time of laser and powder. [Dre16] [DLD15] For those reasons, the laser energy input with expanded laser spot is investigated during this research in order to achieve a high surface exposing speed with a simultaneously low scanning speed. The goal is a gentle, fast and homogenous energy input into the powder.

Experimental set-up

In order to qualify new materials for the laser sintering process, a SLS test equipment has been developed at the University of Paderborn in collaboration with the company PROTIQ GmbH. An overview of the new SLS machine is shown in Figure 1. The maximum build space is 200 x 250 x 300 mm³. To save powder material, it is optionally possible to work with a reduced build chamber with the dimensions of 100 × 100 × 100 mm³. The powder can be coated with the conventional solutions blade or roller and with an innovative powder application system for grinded powders with poor free-flowing properties.

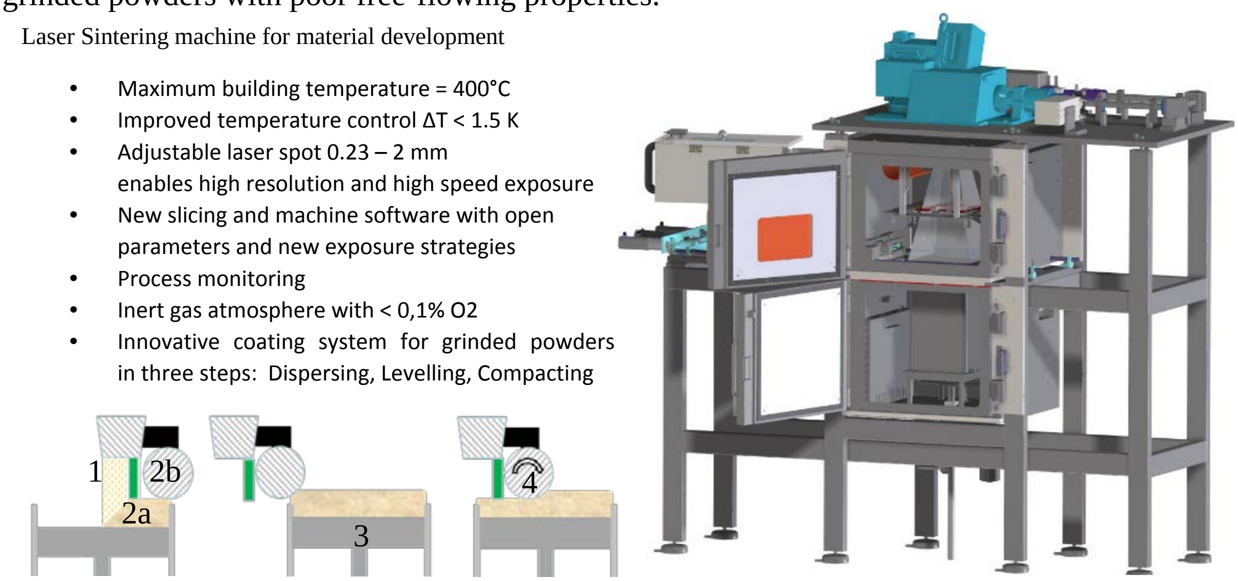


Figure 1: SLS test equipment for material qualification
(Developed at Paderborn University in collaboration with the PROTIQ GmbH)

This newly developed coater operates in three steps displayed in Figure 1: The process step Dispersing (1) dissolves existing agglomerates and improves the flow behavior. Poorly pourable powder is rubbed mechanically through a sieve with a mesh of 150 µm. Vibrations can also be introduced to prevent the sieve from plugging. A doctor blade (2a) or a counter-rotating roll (2b) distributes the powder uniformly over the powder bed. Finally, a roller compresses the powder to the required powder density (3). In order to avoid an entrainment of oxygen and a cooling of the powder surface by the new powder layer, the powder is pre-heated in the supply container and stored under nitrogen atmosphere. A residual oxygen content of <0.1% is ensured. In order to enable an efficient and highly precise heat transport, the emission behavior of conventional and alternative beam sources was considered and compared to the absorption behavior of polyamides.

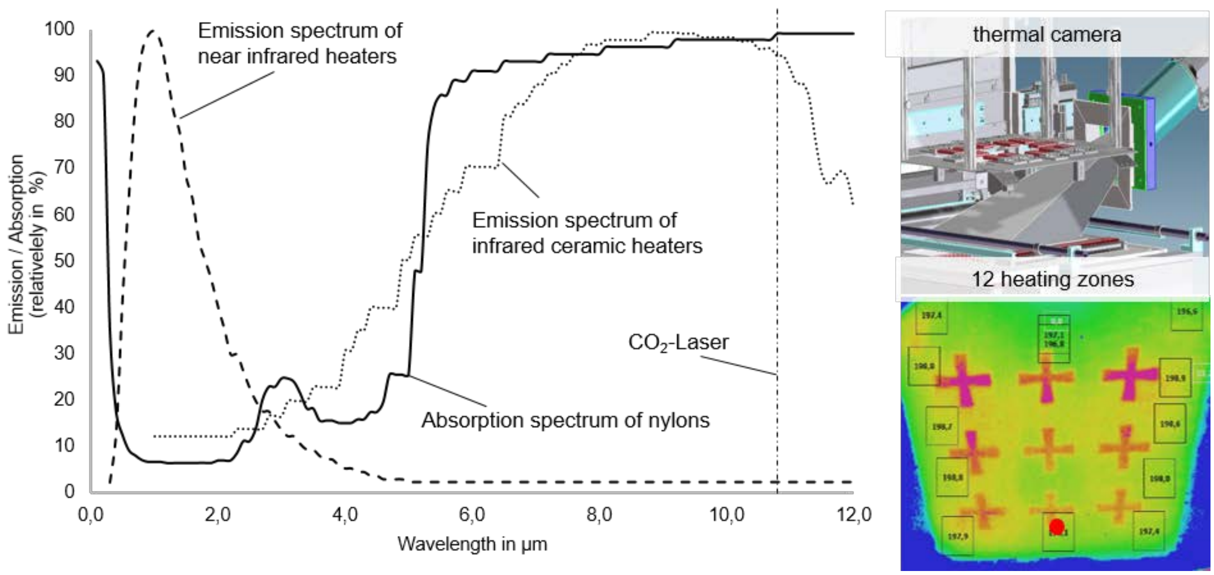
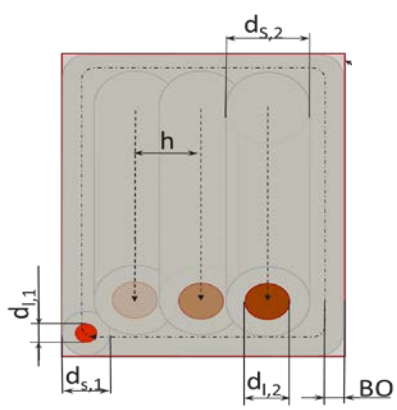


Figure 2: Selection of convenient radiant heaters for efficient heating of nylon materials [Bac16] [Her16] [Tru06]

It becomes clear that the emission maximum of ceramic heaters coincides with the wavelength of the laser and the absorption maximum of polyamides. In contrast, the emission maximum of conventionally used near infrared heaters is arranged in the short-wave infrared area and a considerable portion of the heat radiation is not absorbed by the powder surface. The partial reflection of the heat radiation and the rejected heat of the powder surface and the radiant heaters result in unintended warming of the entire installation space. As a result 12 infrared ceramic heaters are integrated into the developed machine and 12 individual heating zones are realized. The temperature distribution on the powder surface can be measured with an infrared camera and with a pyrometer. The pyrometer can be operated with a static measuring point as well as with a movable measuring spot. In order to move the measuring spot, the pyrometer is integrated into the beam path of the laser system by a beam splitter. The pyrometer and the thermal camera are protected against scattered radiation of the CO_2 laser (10.6 µm) by optical filters. The pyrometer, Kleiber Infrared 660/5, measures the wavelength in a range from 4.7 - 5.2 µm. The measuring range of temperature is 30-500 ° C with a measurement uncertainty of <0.1%. [Kle13] The thermal imaging camera, Optris PI450 GA7, measures the wavelength of 7.9 µm. The measuring range is 200 ° C to 1500 ° C. In the extended measuring range from 0 ° C to 250 ° C it can be measured with a reduced absolute accuracy. In order to allow an accurate measurement at lower temperatures, the pyrometer is added as a reference. [Opt16] Furthermore the position of the heating elements can be selected freely. By separately activating each individual heating element, the specific, effective range can be identified and assigned to an individual measuring field of the thermal camera. The size and position of the measuring fields is freely configurable in the machine software. The measuring fields are marked with black frames in Figure 2. With a sampling rate of 80 Hz, the average value is calculated from each measuring field and sent to the closed-loop control. The twelve-zone control ensures a uniform powder surface temperature with an accuracy of +/- 1.5 K. The maximum temperature is 350 °C.

As explained before, the build up speed in the SLS process is getting more and more important with the increasing use of SLS for series production. An optical system, called Variospot, was therefore integrated into the machine. The Variospot allows the laser spot diameter to be freely adjusted within a range of 0,23 – 2 mm for each line during the exposure [Sca17]. In addition to the variable spot diameter, the focus shift is compensated and a F-Teta Lens is no longer required. The use of the adjustable laser spot offers new exposure possibilities, which are illustrated in Figure 3.



$d_{l,1}$: laser spot diameter in contour line

$d_{s,1}$: melt pool diameter in contour line
(depends on exposure parameter and material)

$d_{l,2}$: laser spot diameter during area exposure

$d_{s,2}$: melt pool diameter during area exposure
(depends on exposure parameter and material)

h : distance between filling-lines

BO : Beam offset between part contour and laser trace

Figure 3: New exposure strategies with variable laser spot diameter

Due to the variable laser spot, complex geometries with thin walls and corners, can be exposed with a small spot diameter and low laser power. In case of large areas exposure is carried out with a large spot diameter, large hatch distance and high laser power. This exposure strategy allows the production of filigree parts at high build-up rates. The scanning speed and the associated scanner delays are reduced and lead to faster exposure times in total. The developed slicing and machine software enables the automatic application of new exposure strategies to CAD models.

When processing new materials, dust formation and outgassing can appear during the process. The optics are protected by a zinc-selenium laser window, which can be cleaned during the process by means of a quick-cleaning system. Additionally the laser-window is continuously cooled and protected by an inert gas curtain.

Experimental Design

First, the function of the test setup is validated. For this purpose, the required process parameters for the standard material PA2200 are determined and compared to results from literature. Next, the new laser sintering powder Vestosint PA6X is considered. As a basis for the subsequent sintering experiments, the particle size distribution, the particle morphology and the thermal material behavior are analyzed. Finally, the material behavior of PA6X is investigated in the sintering process. For this purpose, a uniform powder coating is attempted at first. Subsequently, the process window, determined in the first series of tests, is checked by sintering tests and the building temperature is identified. Based on this, the laser exposure is examined and the required laser energy density is determined. The aim is to achieve high mechanical characteristic values and a robust SLS-process.

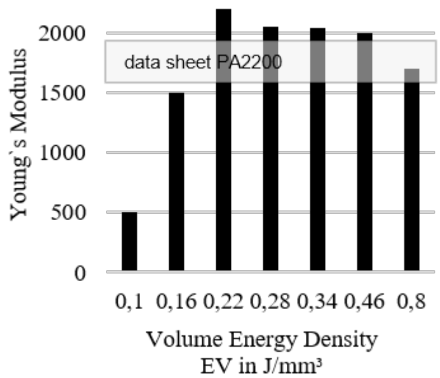
Results

In order to test the functionality and stability of the experimental SLS machine, the standard material PA2200 is processed and the results are compared with literature values. For this purpose, tensile specimens with different exposure settings are manufactured and tested in order to identify the required laser energy density. For the tensile test, five tensile bars are placed in a plane with identical exposure settings. Based on sintering tests, a building temperature of 176 ° C is identified. In order to vary the laser energy input, the laser power is variable. The exposure speed and distance between filling lines (hatch distance) is kept constant. Table 1 shows the exposure parameters. The tensile specimens are tested immediately after the building process in order to avoid time-dependent influences such as water absorption.

Table 1: Exposure parameters: Preheat temperature: 176°C, Material PA2200, Layer 0.1 mm

	Energy density E_V / J/mm³	Laser power P / W	Scanning speed v / mm/s	Hatch distance h / mm	Spot Diameter d / mm	Layer thickness t / mm
Contour	0.7 (P/v*t*d)	8	500	--	0.23	0.1
Filling / Hatch	0.1 (P/v*t*h)	8	2500	0.3	0.5	0.1
	0.16 (P/v*t*h)	12				
	0.22 (P/v*t*h)	17				
	0.28(P/v*t*h)	21				
	0.34 (P/v*t*h)	26				
	0.46 (P/v*t*h)	35				
	0.8 (P/v*t*h)	60				

The results of the investigation are shown in Figure 4. The correlation between the tensile modulus of elasticity and the selected energy density is shown on the left. As explained by Grießbach, an energy plateau that leads to robust mechanical properties is characteristic for the material PA2200 [Gri12]. This energy plateau is reached from a volume energy density of 0.25 J / mm³. Wegner describes an energy plateau of 0.3-0.35 J / mm³ for PA2200 [WW13]. In our investigations, an energy plateau in the range of approximately 0.22-0.40 J / mm³ was identified. For subsequent experiments a volume-energy-density of EV = 0.3 J / mm³ is used, to identify the mechanical characteristics by tensile tests.



	Data sheet PA2200	Results of study EV = 0,3 J/mm³
Powder Density DIN EN ISO 1183	> 0.43 g/cm³	0.442 g/cm³ +/- 0,5%
Part Density DIN EN ISO 1183	0.9-0.95 g/cm³	0.966 g/cm³ +/- 4%
Young`s Modulus DIN EN ISO 527	1700 +/-150 N/mm²	2000 +/- 100 N/mm²
Tensile Strength DIN EN ISO 527	45+/- 3 N/mm²	> 50 N/mm²
Elongation at Break DIN EN ISO 527	20 +/- 5%	12 +/- 3 %

Figure 4: Results of parameter study with PA2200

In Figure 4 the function of the developed SLS machine is validated by comparing the results of the parameter study with values from the product data sheet of PA2200. The table shows that the exposure parameters of the experimental machine lead to similar mechanical properties.
A higher modulus of elasticity and an increased tensile strength are noticeable in combination with a reduced tensile elongation. This effect may be due to the testing without conditioning. With the absorption of water, typically the modulus of elasticity and tensile strength decrease while the values of the tensile elongation increase.

In the next step tests with the new SLS powder material Evonik PA6X are performed. Figure 5 compares the particle morphology of the investigated PA2200 and PA 6X. The chemically precipitated materials, PA 2200 and PA 6X, are characterized by rounded particles with high sphericity.

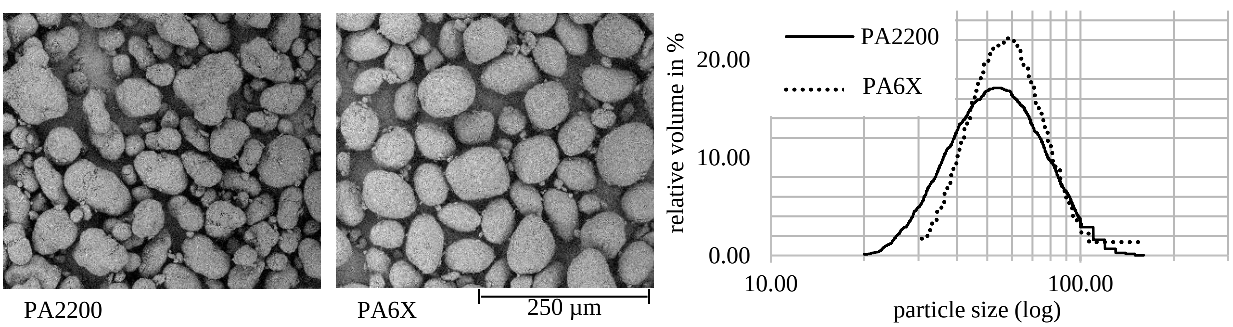


Figure 5: Particle morphology and particle size distribution of the investigated materials PA2200 and PA6X

In addition to the particle morphology, the particle size distribution has a considerable influence on the flow and application behavior during powder application in the sintering process. If the particle size distribution is wider, a poorer flowability results, even if the median value of the particle size is equal [Sch14]. The particle size distribution in Figure 5 was determined by means of laser diffraction with the measuring device Mastersizer 2000 from Malvern Instruments. Based on the results a high powder flowability and a smooth powder surface after coating can be foreseen.

Within the scope of the powder characterization, the material-specific thermal behavior is also examined by means of dynamic differential calorimetry. The thermal behavior of the materials is tested according to DINISO / DIN 11357. A heating and cooling rate of 10 K / s is selected. Based on the results in Figure 6 the required preheating temperature for PA6X can be estimated to be in the range of 185 – 200 °C.

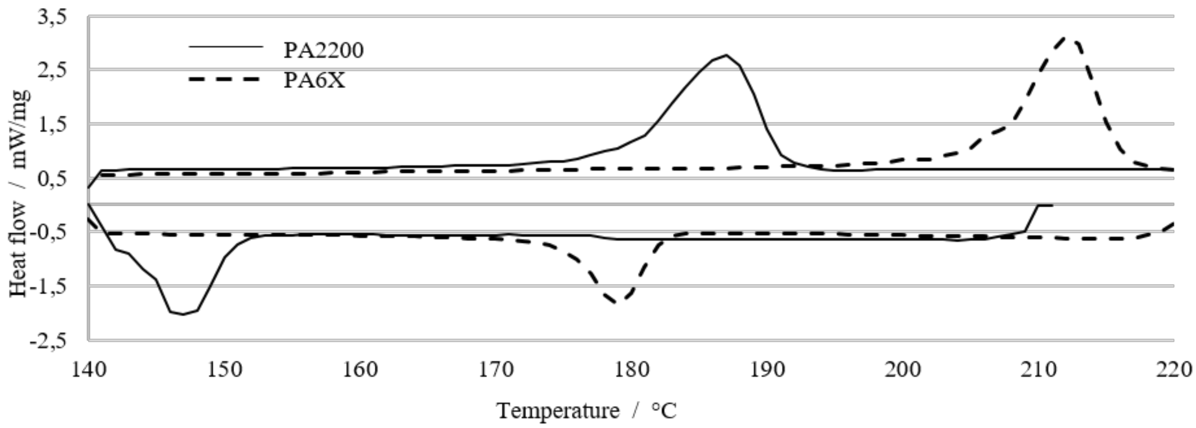


Figure 6: Thermal behavior of PA2200 and PA6X – Measured with dynamic differential calorimetry (DINISO / DIS 11357)

Analogously to the test procedure with PA2200, the new material PA6X is processed. Table 2 shows investigated exposure parameters. The manipulated variable for varying the energy is the laser power. The PA6X powder has good free-flowing properties and can be applied with the conventional doctor blade solution. A layer thickness of 0.1 mm and a coating speed of 50 mm / s is chosen.

Table 2: Exposure parameter study for PA6X

	Energy density E_V / J/mm³	Laser power P / W	Scanning speed v / mm/s	Hatch distance h / mm	Spot Diameter d / mm	Layer thickness t / mm
Contour	0.86 (P/v*d*t)	10	500	--	0.23	0.1
Hatch / Filling	0.27 (P/v*t*h)	8	2500	0.3	0.5	0.1
	0.32 (P/v*t*h)	12				
	0.35 (P/v*t*h)	17				
	0.37(P/v*t*h)	21				
	0.40 (P/v*t*h)	26				
	0.47 (P/v*t*h)	35				

On the basis of the DSC analysis, a large temperature sintering window was identified and confirmed in the experiment. The determined building temperature is 192 ° C. The sintering process is stable and robust in a range of temperature from 188 °C up to 195 °C. The white color of PA6X is similar to sintered parts out of the material PA2200. Very filigree models can be realized and the residual powder does not tend to cake. With the minimum laser spot of 0.23 mm a wall thickness of 0.23 mm can be achieved. Figure 8 shows that the required energy plateau for the material PA6X is reached at a laser volume energy density level of 0.35 J / mm³. From an energy density of > 0.4 J / mm³, the tensile strength begins to decrease, because of degradation.

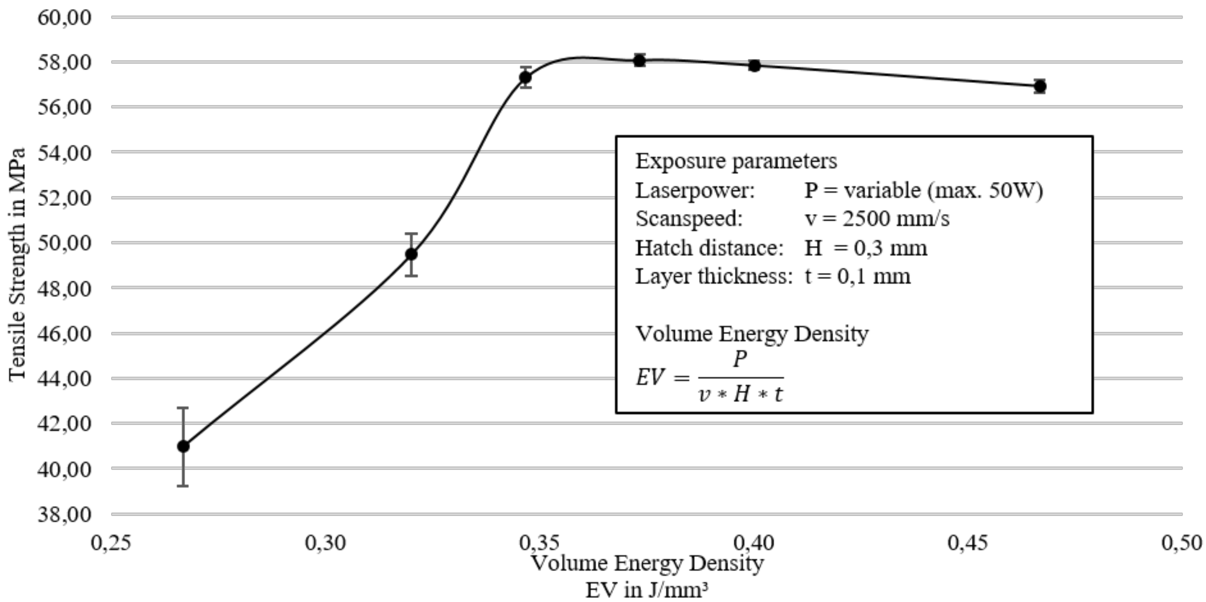


Figure 7: Tensile strength as a function of Laser Energy Density during exposure

Conclusions & Outlook

An SLS system was developed for the qualification of new LS materials. The main benefits of the SLS test equipment are an optimized temperature management, an innovative powder application for grinded powder materials and a freely adjustable laser spot diameter. All machine and process parameters can be selected freely inside the developed slicing and machine software.

The function of the system technology was validated with the known material PA2200 from EOS. For this purpose tensile specimens were built and the volume energy density of the laser exposure was varied. The necessary energy level for a robust process management was identified. The obtained mechanical characteristics correspond to the data in the material data sheet of the manufacturer EOS for PA2200.

In addition, the new SLS material PA6X was processed. PA6X is characterized by good processability. The highest tensile strength of 58 MPa was achieved with a laser power density of 0.37 J / mm³. The material PA6X stands out against the standard material PA2200 by a higher temperature resistance and a high elongation at break > 25 %.

In future work, the effect of different exposure strategies will be investigated and a statistical tests will be used to confirm the gathered mechanical properties. In particular, the influence of a variable laser diameter on the material properties has not yet been conclusively investigated. In order to make comparison with existing laser sintering systems with a constant laser spot diameter possible, the area exposure rate with the unit mm² / s can be an interesting characteristic parameter. The laser exposure time per unit of area at identical surface speed might be increased by the exposure with an expanded laser spot. It is known from injection molding that, compared to polyamide 12, polyamide 6 absorbs significantly more moisture after the manufacturing process, thereby mechanical properties and dimensions can change. For this reason water intake and its influence on the mechanical characteristics should be investigated. So far the thermal behavior has been determined by means of DSC analysis. For the design of serial products, mechanical properties will be determined as a function of the application temperature.

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