A MATERIAL-BASED QUALITY CONCEPT FOR POLYMER LASER SINTERING

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Abstract

In this work, the quality of laser sintered parts is investigated along a defined process chain for a nylon 12 material (PA 2200) on an EOSINT P395 laser sintering system. Important influencing factors are figured out. Rheological powder characterization methods are investigated as well as mechanical, physical and other chosen part properties. The concept allows reproducible part quality characteristics and is used to obtain (testing) temperature dependent material data. It can also be extended on further materials based on nylon 12: PA 2241 FR, which is convenient for the aircraft industry due to its flame-retardant properties, and PA 2221, which has economic advantages due to a lower material consumption.

Introduction

With Additive Manufacturing (AM) technologies it is possible to manufacture parts directly from given CAD data. Usually, the parts are generated layer-by-layer. One of the most important AM technologies is Polymer Laser Sintering [Woh13]. Thereby, a polymer powder is molten by a laser that scans the part's contours onto a thin powder layer. However, the quality of laser sintered parts varies due to a multitude of influencing parameters and the lack of AM process and quality standards [SL12].

Qualification, verification and validation are important aspects to approach this challenge. Reliable material data sets are necessary for the dimensioning of technical parts; the development of a quality standard is vital for reproducible manufacturing processes to obtain the expected part properties.

The work in hand describes a concept for steady part quality characteristics. Important influencing factors are figured out along a quality chain for the laser sintering process. Measures are deduced to keep these factors constant. Starting with nylon 12 (PA 12, EOS PA 2200), material data is gained regarding a variety of part quality characteristics. Later, further materials are tested in the same way and compared reliably.

State of the Art

The quality of parts manufactured using Polymer Laser Sintering (LS) has been investigated in many scientific studies and works. "Quality" depends on the individual requirements of an LS part. Criterions can be the mechanical behavior as well as the surface quality, warpage or physical properties like the part density or the electric resistance. The main challenge is to know and control the process parameters and their influence on these quality criterions. An overview and a systematic classification of important influencing parameters on powder-based Additive Manufacturing processes in general was given by Schmid and Levy in [SL12], Figure 1.

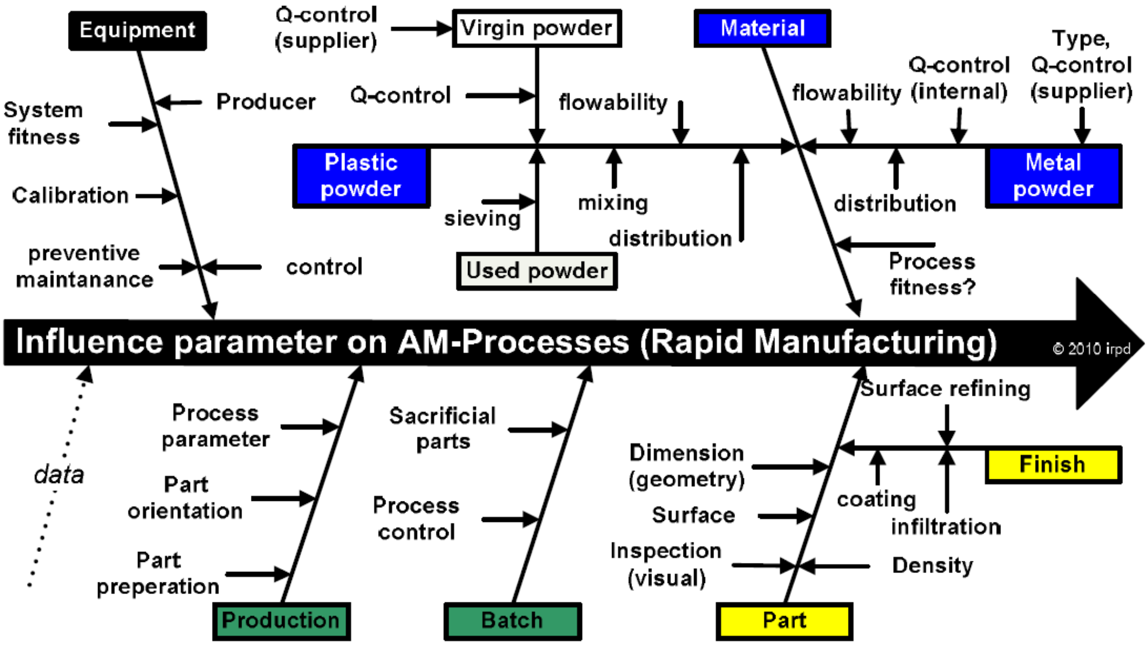

Figure 1: Parameters of the AM process production chain [SL12]

The influencing parameters can be classified into the Equipment, (plastic) Powder, Production/Batch and Part/Finish. Regarding powder characterization, especially the powder bulk flow properties, the viscosity and the melt flow behavior of polymer powder has been in the focus of many research projects. For example, Amado et al. investigated the flowability of different powders to characterize the suitability of materials for the LS process [ASL+11]. A link between powder age and rheological properties was made by Rüsenberg et al. using the melt volume rate and the solution viscosity to characterize the thermal loading of used powder [RWF+12]. Also, the influence of these powder properties on several part properties has been investigated, for example the mechanical behavior and the surface quality. Another way to characterize polymer powders is the thermal analysis. Drummer et al. used the Dynamic Differential Scanning Calorimetry (DSC) to investigate phase transitions while heating (melting) and cooling (crystallization) different LS materials [DRK10]. Later, these results were used to analyze the impact of the heating rate on LS part densities [DDW+13].

The most important influencing factors regarding the production (LS process) are the part orientation and process parameters, for example the energy density, process temperatures, scanning strategy or the cooling procedure. Many different investigations show the influence of these parameters on the quality of LS parts. For example, Rüsenberg et al. changed the laser energy density to analyze its influence on the LS part density, shape and mechanical properties [RSS11]. The process temperature within the building plane was investigated by Wegner et al. using thermal imaging [WW11] and later correlated with mechanical and physical part properties [WW13]. It was found out that an inhomogeneous temperature distribution leads to varying part qualities at different positions within the building area. Although many part quality characteristics can be adjusted by changing different process parameters, their large variety can lead to inconsistent part properties. To create a standard of process parameters and to increase the reproducibility of build jobs, the LS system manufacturer EOS developed the Part Property Profiles (PPPs), which are sets of fixed parameters, connected to a specific layer thickness. Furthermore, it has to be considered that different powder and process parameters may correlate or influence each other.

LS Process Quality Chain

Based on past research projects at the Direct Manufacturing Research Center (DMRC), an LS Process Quality Chain was developed based on a wide range of pre-tests described in past publications. Considering as many influencing factors as possible, reproducible and application-oriented material data sets are obtained. Therefore, also the testing procedure (experimental set-up) is included. The Process Quality Chain is given in Figure 2.

Figure 2: LS Process Quality Chain [RS13]

The data preparation is the first step of the LS Process Quality Chain and vital for general part properties. A sufficient STL data quality is an important prerequisite. Due to the fact that the weakest properties are always obtained in z-direction (orthogonal to the build layers), the orientation of an LS part in the build chamber must be selected considering given load cases for the parts in application. Another aspect is the part placement. As mentioned before, part properties can vary due to different temperature histories at different places within the building frame. The hatch line conformity (number of hatch lines per part layer) must also be constant for reproducible results.

The material, particularly the state of the used material and the mixture ratio of used and virgin powder is one of the most crucial factors within the quality chain. Since the exact degree of ageing (thermal loading) cannot be known for every build job, the mixture ratio itself is not sufficient to ensure a constant powder quality. Measurements of the Melt Volume Rate (MVR) have been proven as a suitable means for a characterization of mixed powder, although there are many other possible criterions like the flowability, viscosity, thermal behavior or the molecular chain length.

Regarding the LS process, the laser parameters (intensity, speed, scanning strategy…) have a big influence on different quality aspects. Furthermore, the temperatures within the building and removal chamber have to be kept constant during the building process. The type of the LS machine and its technical condition (routinely maintenance and calibration) has to be considered as well as long enough heating up and cooling down times. After unpacking and sieving the part cake, a post treatment (blasting, coating…) is especially influential on the surface properties.

In this work, the build jobs of the described experiments have all been designed considering the described factors to gain a highest possible material data quality. Therefore, concrete measures as result of the LS Quality Chain Concept were figured out and are described in the following (Figure 3). Since there is only a slight material dependency of the measures (only the build temperature and the Part Property Profile), different materials can be tested and compared reliably.

Data Preparation	Material	Pre-Process / Machine
- study of the weakest (z) and strongest (x/y) orientation - packing in the inner area of the building frame (50 mm distance from edges) - constant number of hatch lines per (same) part	- known powder history - representative powder age (“circulatory powder”) - known virgin/aged powder mixture ratio adjusted by MVR value	- newest equipment - controlled laser power and temperature distribution - regular maintenance, cleaning and calibration - strorage of material and machine in standard atmosphere
LS Process	**Post-Process**	**Testing Process**
- EOS Part Property Profiles (PPPs) → build parameters - layer thickness 60 – 180 µm - 4h preheating time - 10h cooling time within machine (nitrogen) - min. 24h cooling time outside machine (<50°C)	- defined blasting process (time, pressure, distance → automatic blasting system) - conditioning of specimen in standard atmosphere (min. 4 weeks) OR - dry tests (shrink-wrapping of specimen until tests)	- testing of material - testing of parts - detection of links between material and part properties - …according to international test standards (DIN EN ISO)

Figure 3: Extract of measures for reproducible part quality characteristics

Material & Part Characterization Methods

Job Layout

The Job Layout shown in Figure 4 consists of tensile, flexural and pressure test specimens for mechanical part testing and powder boxes to determine the powder properties at defined places within the part cake. The Job is built up hatch-compliant and considering shrinkage and overcure effects, so that the specimen’s dimensions fit into the tolerances of the test standards.

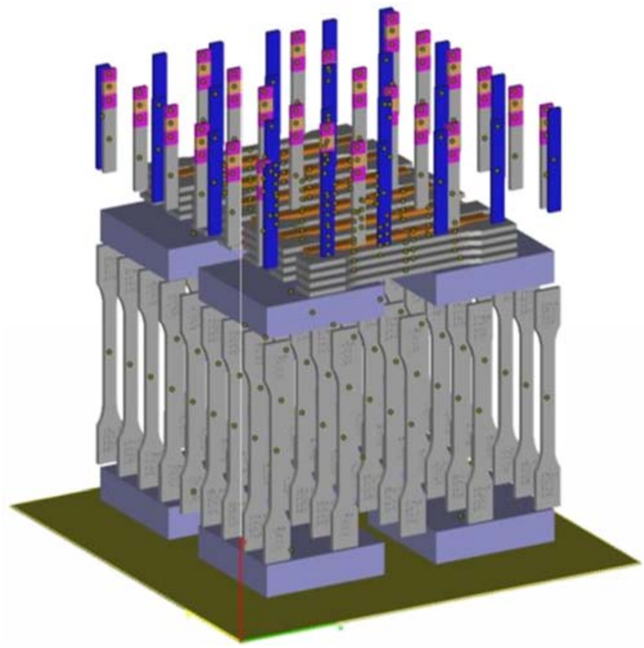

Figure 4: Job layout for testing temperature- and layer thickness dependent part tests

The jobs have been built up with 60, 100, 120, 150 and 180µm layer thickness using the EOS Part Property Profiles for the respective material. Therefore, recoater blades with different blade shapes were used: A flat blade for 60µm, a circular blade for 100 and 120µm and a triangular blade for 150 and 180µm. These have an impact on the powder compression during recoating the layers. All Jobs were performed on an EOSINT P395 Laser Sintering System with one representative batch of mixed powder adjusted by an MVR of 31 cm³/10min. For unpacking and sieving, the appropriate unpacking station was used.

Melt Volume Rate (MVR)

The Melt Volume Rate (MVR) is a method to analyze the melt flow of thermoplastic polymers and can be used to predict the process behavior of the material. Therefore, a specific amount of powder is molten in a heated tube and then pressed through a defined tip under a load applied with a piston. The velocity of this piston finally gives the information about the flowability of the molten material. The higher the thermal loading of the material, the lower is the MVR value. The unit of the MVR value is cm³/10min.

For these examinations on nylon 12 based materials, 4g of powder was filled in the tube and heated up for 300s at 235°C. The load on the piston was 5kg and the measurement length was 14,6mm. A measurement device of the manufacturer Zwick GmbH (mod. "Mflow"), Germany, was used. To predry the material, the samples were treated in an unconditioned furnace (mod. "Thermo Scientific UT 6") for 10 min at 105°C, 5 min at 105°C to 140°C and 2 min at 140°C. This testing procedure is based on the test standard DIN EN ISO 1133.

Tensile, Flexural and Compression tests

The mechanical properties of the LS parts were determined with an Instron Universal testing system 5569 with an attached environmental chamber to apply temperatures between -60°C and +90°C on the specimen. Liquid nitrogen was used to cool down the camber below room temperature; heating was applied electrically. The force was measured with a 5 kN load cell.

Tensile tests were performed according to the test standard DIN EN ISO 527. The strain was measured contactless with an Instron Advanced Video Extensometer (AVE). The dimension of specimens within the measurement length was 4 x 10 mm². Measurement results were the Young's modulus, the tensile strength and the strain at break. The truss speed was 1 mm/min for the determination of the Young's modulus and 50 mm/min for the further values.

The flexural properties were obtained using a three-point-bending apparatus with a span length of 64 mm according to test standard DIN EN ISO 178. The dimension of the specimen was 4 x 10 x 100 mm³; the truss speed was adjusted to 2 mm/min. Flexural strength properties were analyzed as well as the flexural modulus and the strain at break (if broken before maximal possible deflection).

To detect the compression behavior, the test standard ISO 604 was used. The specimens have a cross sectional area of 4 x 10 mm and two different lengths: 50 mm for the compression modulus (truss speed 1 mm/min) and 10 mm for the compression strength (truss speed 5 mm/min). Since the material blocks the movement of the compression plate and the strength rises continuously, the compression strength was defined as the strength at a strain of 20%.

Powder Bed Density (PBD)

The powder boxes were measured with a standard digital caliper; the unmolten material was extracted and weighted on a Mettler Toledo XS4002S digital balance. Divided, these values give information about the density of the powder bed.

Moreover, the material was additionally analyzed using the Differential Scanning Calorimetry (DSC) and the Gel Permeation Chromatography (GPC) to obtain information about the impact of the thermal loading on the melting/crystallization behavior and on the molecular chain length at different places within the part cake. Another test was performed to analyze the solution viscosity of nylon 12 solved in m-Kresol (Ubbelohde low-pressure viscosimetry). However, these tests are not subject of this paper.

Results for PA 2200

The given job layout was at first built 6 times with a layer thickness of 120 µm to examine the reproducibility of quality criteria. Therefore, 9 tensile specimen (z direction) were extracted from every build job at defined positions and tested dry. Since the specimen for the different testing temperatures originate from different build jobs, this is important for a reliable comparison of measures. The results of these dry specimen are shown in Figure 5. The tensile strength seems to be the most robust value with an average of 50.73 MPa and a standard deviation of 0.83 (1.6%). However, the values of the Young's modulus are more volatile with an average of 1994 MPa and a standard deviation of 170 MPa (8.5%). Also the elongation at break (not shown in this figure) has higher deviations in reproducibility (average: 9.51%, standard deviation: 1.87% (19.6%)).

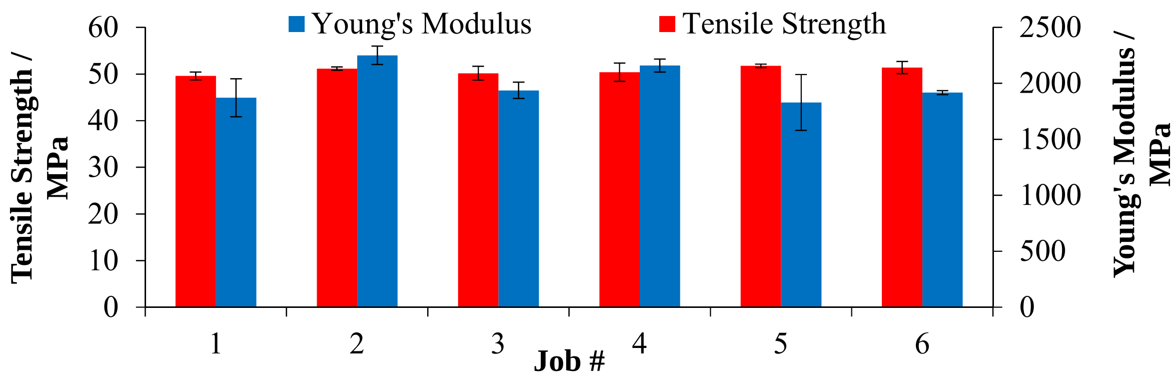

Figure 5: Reproducibility of mechanical part properties (120 µm, dry specimen)

The following figures 6 to 8 show the results of the temperature-dependent tensile, flexural and compression strength properties for 120 µm layer thickness and different build directions. For every loading condition, the strength decreases from low to high temperatures. Beginning from room temperature, the tensile strength increases by approximately +43% at -50°C (ΔT = -70 K). For the flexural strength, the enhancement is about +77% and for the compression strength it is approximately +53%. Similar changes of strengths can be observed for higher temperatures: Starting at room temperature, the strength decreases by about -49% for tensile, -53% for flexural and -46% for compression specimen at 90°C (ΔT = +70 K). This shows that the flexural properties are the most sensible parameters regarding temperature deviations. However, slight non-linearities must be considered.

Between x and z oriented specimen, differences in mechanical strengths can be observed especially in the tensile strength at low temperatures: The lower the temperature, the lower is the increase of tensile strength for z oriented specimen. For higher temperatures and flexural or compression loading, z strengths are usually only slightly lower compared to the x strengths.

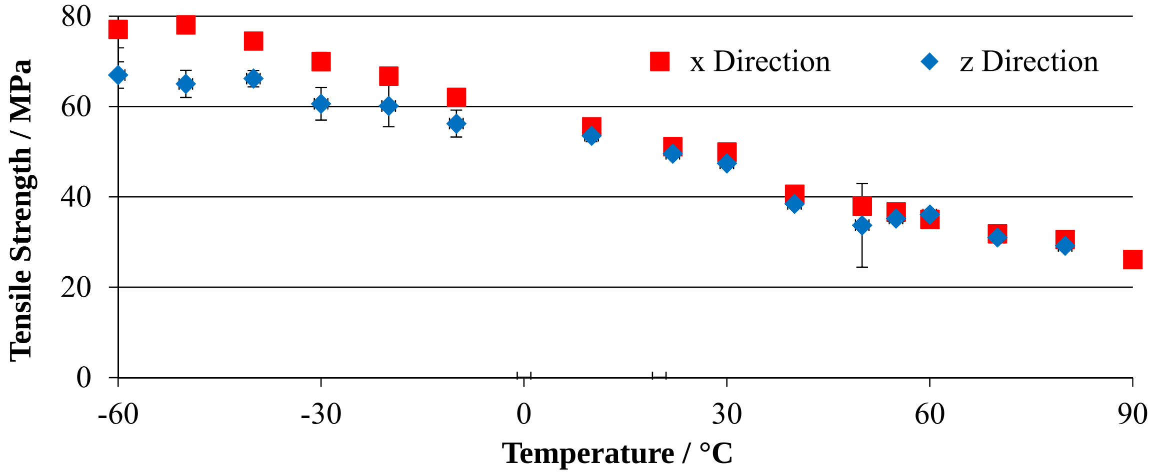

Figure 6: Temperature-dependent tensile strength for 120µm layer thickness

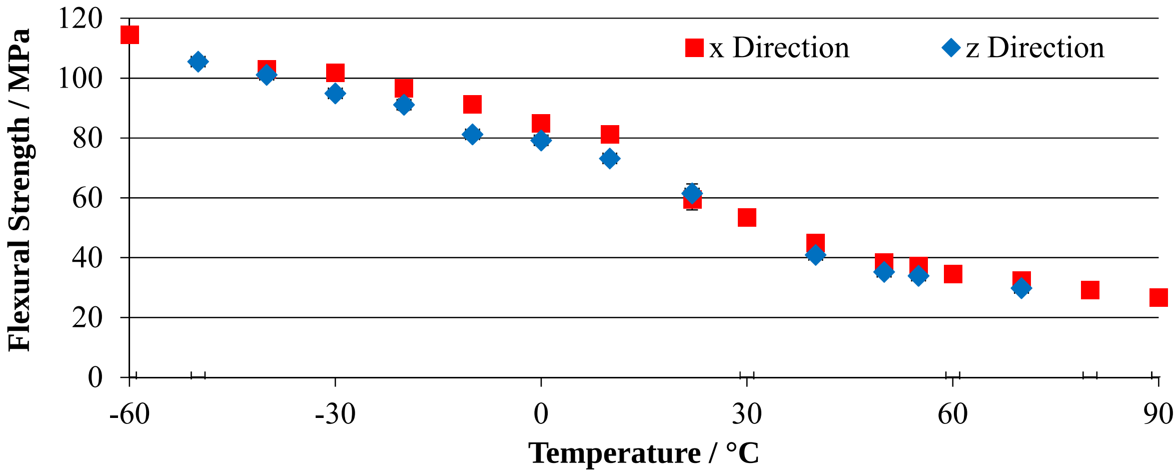

Figure 7: Temperature-dependent flexural strength for 120µm layer thickness

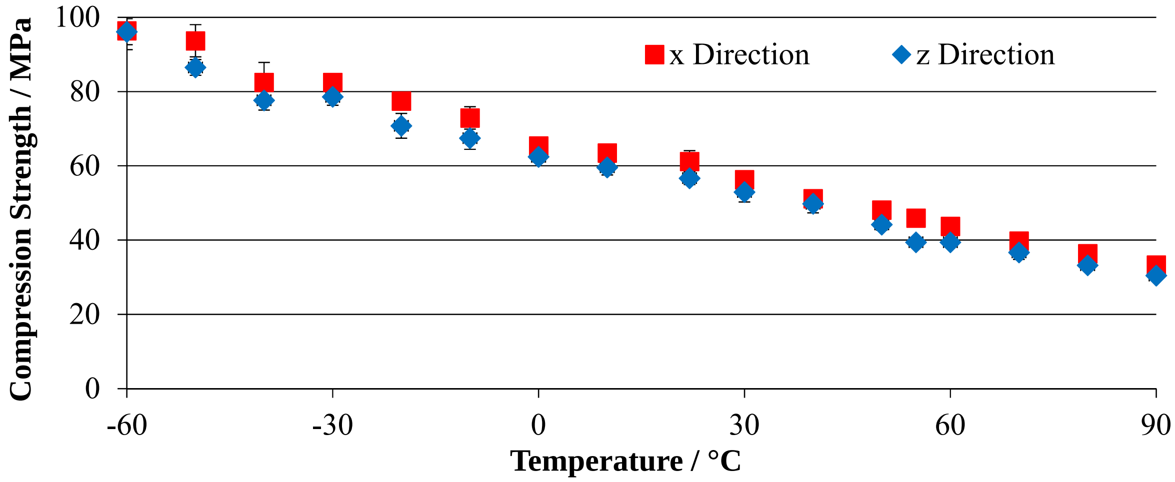

Figure 8: Temperature-dependent compression strength for 120µm layer thickness

Although it was shown that the modulus is a less reproducible parameter, it is a very important value in dimensioning of parts. To show the temperature-dependency of the specimen stiffness, results for the Young's (flexural) modulus are shown in Figure 9. The behavior of the material can be divided into three areas: The majority of the deviation can be observed between 0°C and 60°C, at lower and higher temperatures the Young's modulus is nearly stable. Thus, a variation of temperature in this "middle" area results in significant changes of the flexural stiffness. Also, the diagram shows values of the flexural modulus for different layer thicknesses. However, no significant layer thickness dependency can be observed.

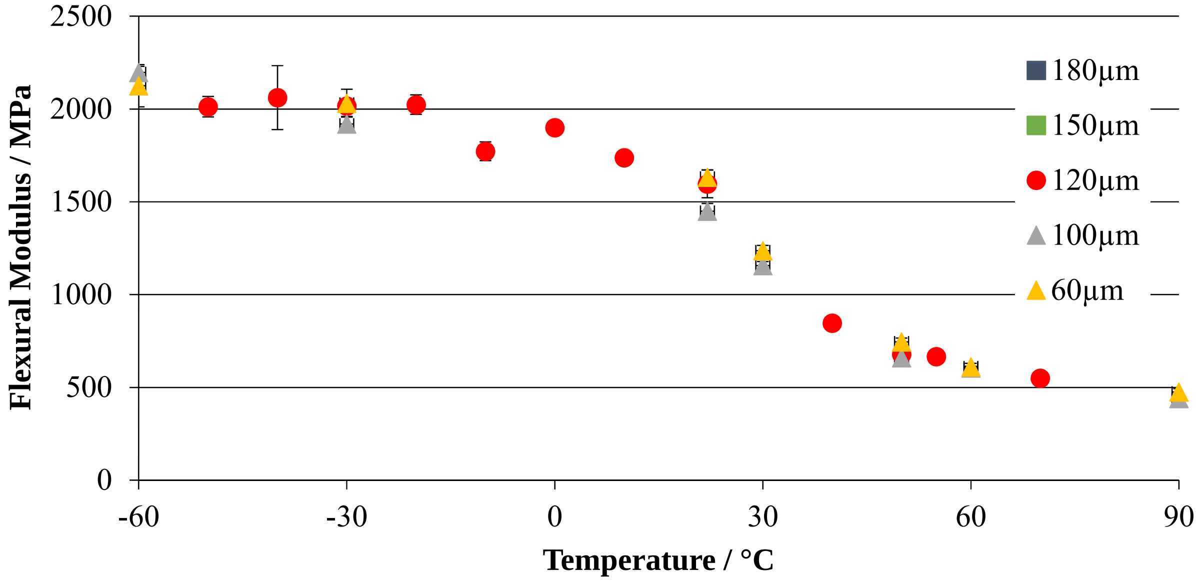

Figure 9: Temperature-dependent flexural modulus for different layer thicknesses (z direct.)

The melt volume rate, which characterizes the flowability of the molten material, gives information about the thermal loading of the powder during the building process. The mixed powder used for the build of all test jobs has an MVR of 31 cm³/10min. Figure 10 shows the average MVR values after the building processes for different layer thicknesses and positions within the building frame (the powder was extracted from the powder boxes, see Figure 4). The higher the layer thickness, the higher is the MVR value. As a consequence it can be deduced, that thin layers cause a significant stronger ageing of the material due to a longer build process with a higher energy input. Also, the position within the building frame has a relevant influence on the thermal loading: The center powder boxes contain "worse" powder than the bottom ones. The reason behind is a slower cooling rate in the inner part of the powder cake. At the bottom and at the edges, a higher cooling rate causes less thermal loading and higher MVR values

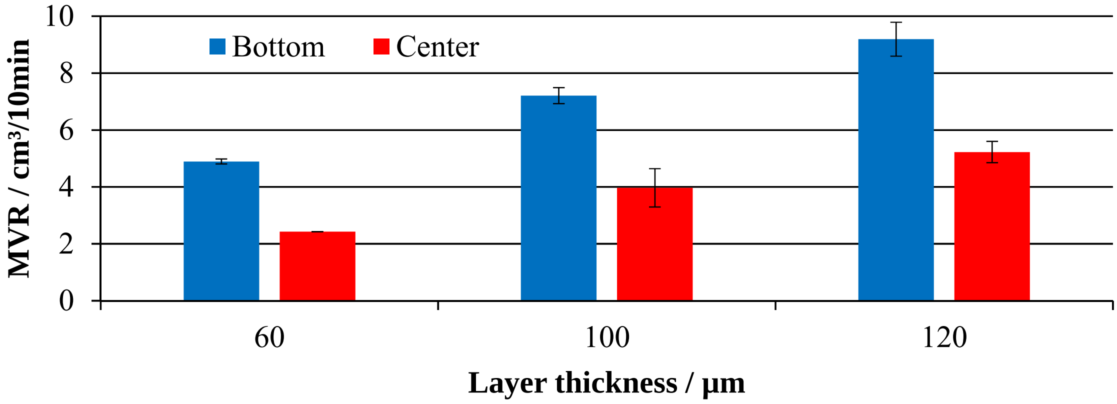

Figure 10: Average melt volume rate (MVR) at different layer thicknesses and positions

The density of the recoated powder is given in Figure 11. The flat recoater blade (60µm) produces the minimal density, whereas the circular and triangular blades cause slightly higher thicknesses. With the same type of blade shape (100/120µm: circular; 150/180µm: triangular), the smaller layer thickness always results in a higher powder bed density. This effect can be traced back to a more intense compression of the powder using small layer thicknesses.

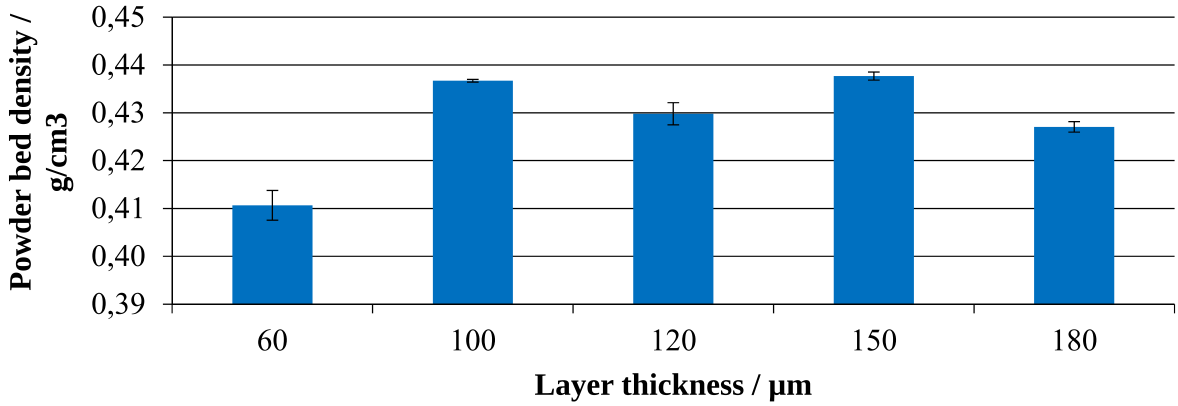

Figure 11: Average powder bed density (PBD) as function of the layer thickness

Application of the methods on PA 2221 and PA 2241 FR

After the building process and testing methods have been proven for the standard nylon 12 material (PA 2200), the series of measurement are repeated with further materials based on nylon 12. In this way, different materials can be compared with a minimal change of the process quality chain. The first experiments have already been conducted for the new flame retardant material PA2241FR. Another material, PA 2221, is optimized regarding the material consumption. Due to a lower refresh rate of about 30%, new pre-tests are necessary in order to obtain material with a representative ageing state. In the following, both materials are described in detail.

PA 2241 FR

PA 2241 FR is a halogen-based flame retardant material based on nylon 12 (PA 12) and is therefore most convenient for the aircraft industry [EOS13]. The main advantages compared to the flame retardant material PA 2210 FR claimed by the manufacturer EOS are passed flammability tests at already 1.0 mm wall thickness, a higher tensile strength and a refreshability of 50% used/virgin material. PA 2241 FR is currently approved for the layer thicknesses 100 and 150 µm. Both parameter sets will be tested and compared to PA 2200.

PA 2221

PA 2221 is also a modified nylon 12 (PA 12) material and allows lower refresh rates of about 30% virgin powder mixed with 70% used (aged) powder. Thereby, the material consumption and the amount of waste can be reduced. Another advantage claimed by the manufacturer is less warpage of the laser sintered parts.

In the first tests, it was found out that virgin PA 2221 material has only a small process window: The parts showed curling effects even at very high temperatures causing a rigid part cake. Thus, a "dummy" job without laser exposure is recommended and was conducted using the same job as described, but with a laser power of 0 W. Mixed with virgin powder again, the process behavior is similar to circulatory PA 2200 powder. Due to the lower refresh rate, the number of runs until the part quality is constant (representative powder) is not known yet. This is the object of current building and measurement series with PA 2221. After the powder can be characterized as circulatory powder, the material can be tested corresponding to the described PA 2200 and PA 2241 FR studies.

To apply the measures of the LS Process Quality Chain on further materials, individual application notes must be considered. For example, there are changed maintenance intervals or the material shows such a different behavior in powder testing, that the testing parameters must be adjusted. However, the change of process steps shall be as small as possible to maintain the comparability.

Summary & Outlook

The measures developed for steady part quality characteristics along the LS Quality Process Chain allow the manufacturing of LS parts with reproducible properties regarding the mechanical behavior. This fact was used to gain a variety of reliable layer thickness and temperature dependent material data using specimen from different build jobs. It was shown how the temperature influences the tensile, flexural and compression strengths and that the stiffness of LS parts is significantly influenced even by slight temperature deviations. Thereby, flexural tests showed the clearest temperature dependency. A measurement of the melt volume rate was used to characterize the thermal loading of unmolten material. It was shown that the layer thickness and the position within the building frame influence the thermal loading of the powder. However, further powder tests will follow in additional studies.

New materials available for the laser sintering processes enable further fields of application for the LS technology. Hence, it is important to know as much as possible about the individual material, part and processing properties to qualify these materials reliably. Therefore, a comparison to proven materials is obvious and – with this concept – possible.

In additional experiments, the quality concept will be expanded to examine further quality aspects, for example the surface and fatigue properties of laser sintered parts. Furthermore, single parameters will be varied to measure their influence on the part quality.

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