

## **Controlling the Quality of Laser Sintered Parts Along the Process Chain**

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### **1 Abstract**

The quality of laser sintered parts, in this work, manufactured by polymer laser sintering by using an EOSINT P395 Laser Sintering system, depends on several steps along the process chain. The first step is the characterization of the powder quality, whereas the rheological and physical investigations of nylon 12 powder are shown. By changing some important influencing factors, for example the powder ratio, the powder ageing and the moisture content, the influence on mechanical and physical properties, density and porosity, are investigated. The composition of the used powder is known. The previous process (storage conditions, etc.) as well as the laser sintering process (regarding energy density, temperature, etc.) is kept constant for the duration of this work. Regarding the post process in this work the cooling down phase is investigated as well. With an automatically blasting system it is possible to keep the post process parameters blasting distance and blasting time, constant. All of the tests will be performed using dry and conditioned test specimens.

This work is showing the dependence on mechanical, rheological and physical parameters by varying important influencing factors along the laser sintering process quality chain.

### **2 Introduction**

Additive manufacturing technologies will be important for different direct manufacturing applications within several industry fields. The study “Thinking ahead the Future of Additive Manufacturing – Analysis of Promising Industries” is giving an overview about possibilities and chances using AM technologies for diverse industries. However, the way to a serial manufacturing process will be a difficult one. Lots of parameters might be known now, but there is lots of work needed to understand them [DMRC12].

An important factor will be the powder quality of the input material. At the moment the material is mixed by using a fixed powder ratio of used and virgin powder. However, the condition of the used powder is typically unknown or at least uncontrolled. There is no information about the age or the thermal loading of the used powder. The thermal loading is influenced by different parameters like number of parts, height of the building job, unpacking behavior, building temperature as well as the temperature within the removal chamber. It is necessary to find a possibility to characterize a parameter for a powder qualification. Therefore it is important to correlate rheological and particle properties with material properties. Often mechanical properties are used as a quality criterion, but there have to be investigations of additional physical, thermal and electrical properties as well. This work is presenting the correlation between mechanical

properties and different powder qualities adjusted by melt volume rate and revised by solution viscosity.

### 3 State of the Art

The research in the field of ageing of nylon 12 and the different influencing factors of the Laser Sintering Process on the material are approached by different methods. A commonly used method is the DSC-analysis, with which the crystalline melting temperature as well as the crystallization temperature of plastics can be determined. The window between these temperatures determines the area in which the plastic can be processed. This window is particularly big for nylon 12, which makes it very good to be used in LS. At the department of plastics technology of the Friedrich-Alexander-University Erlangen-Nürnberg it is shown in research, using artificially aged nylon 12, that the crystal melting temperature as well as the crystallization temperature is increased for aged powder. During these examinations the factor time regarding the structural change of the material was made clear. The longer the material is exposed to thermal stress, the more the structure of the material changes. This can be seen in figure 1, where a DSC-analysis of three differently aged powders is shown [Drummer10] [Gornet02].

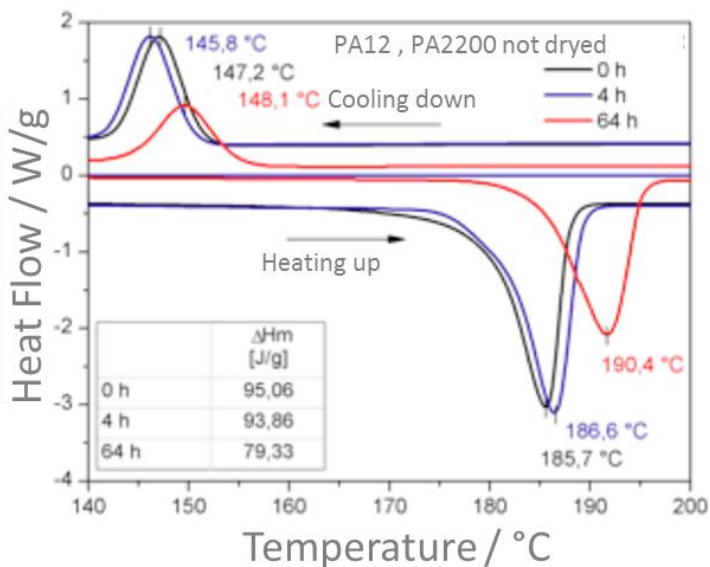


Figure 1: DSC Analysis of nylon 12 [Drummer10]

Altogether the crystalline melting temperature increases more than the crystallization temperature, which results in a wider processing window of aged powder and thus allowing larger fluctuations in the building process than with pure new powder. This fact has to be considered critically regarding the change of the viscosity for old powder, since it is increased and thus influences the processing of the powder and the quality of the parts negatively. Furthermore the smaller peak shows that the needed enthalpy of fusion strongly decreases, which can be traced back to a reduced degree of crystallinity. In addition the melting peak is getting wider, which can be explained by a thermally caused post polymerization or post networking of the chain molecules. The increase of the crystal melting temperature can be further explained by a growth of the spheroids. By post polymerization and post networking of the chain molecules

these can entangle more and form bigger spheroids, which are more resistant to melting [Drummer10][PDY08].

Another method to analyze aged powder is the determination of the MVR (Melt Volume Rate) respectively MFR (Melt Flow Rate). At the Rapid Prototyping Center of the University Louisville it is shown that these values decrease for aged powder. Since the MVR- and the MFR-value are inversely proportional to the viscosity, the viscosity increases for aged powder. These results show that through thermal stress in the LS-process a post polymerization or post networking occurs. This is supported by solution viscosity measurements. Results from these measurements are shown in figure 2. With increasing age the viscosity value of the PA12 increases. The viscosity increases for a growing chain length of the polymer molecules [Drummer10] [Gornet02].

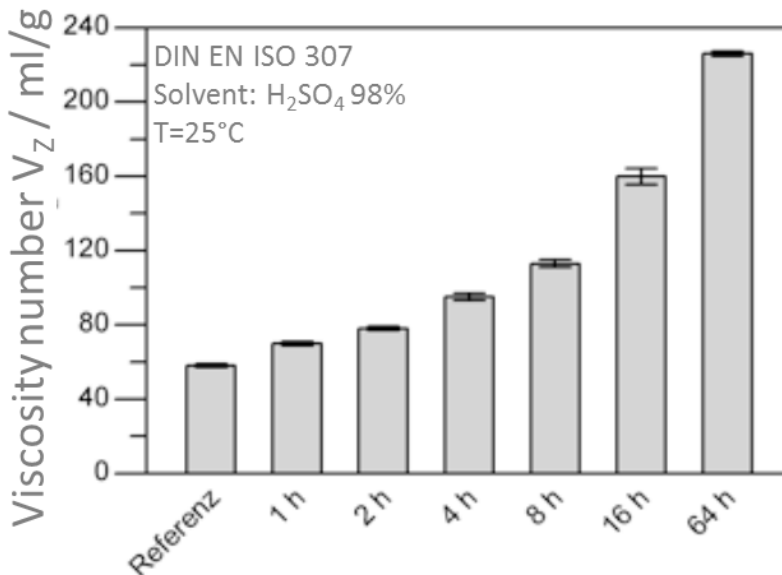


Figure 2: Solution viscosity measurement [Drummer10]

In order to further examine the structural change in the nylon 12, SEC-analyses have been executed. With SEC-analyses a molecular weight distribution can be determined. In addition the molecular weight distribution of sintered parts can be determined, since for the SEC-analyses the powder, respectively the parts have to be dissolved. Results of such an analysis can be seen in figure 3.

The blue curve represents virgin powder and the red curve old powder, passed the laser sintering process twice. It can be clearly seen that the red curve is shifted to the right and gets wider. Regarding the structure of the chain molecules this means that the chain generally lengthens and thus the molecular mass of the molecules increases. Comparing these results with a SEC-analysis of a sintered part, an even higher increase of the molecular mass can be detected, which is logical regarding the stronger thermal stress during the process [ZHKV06] [DMRC12].

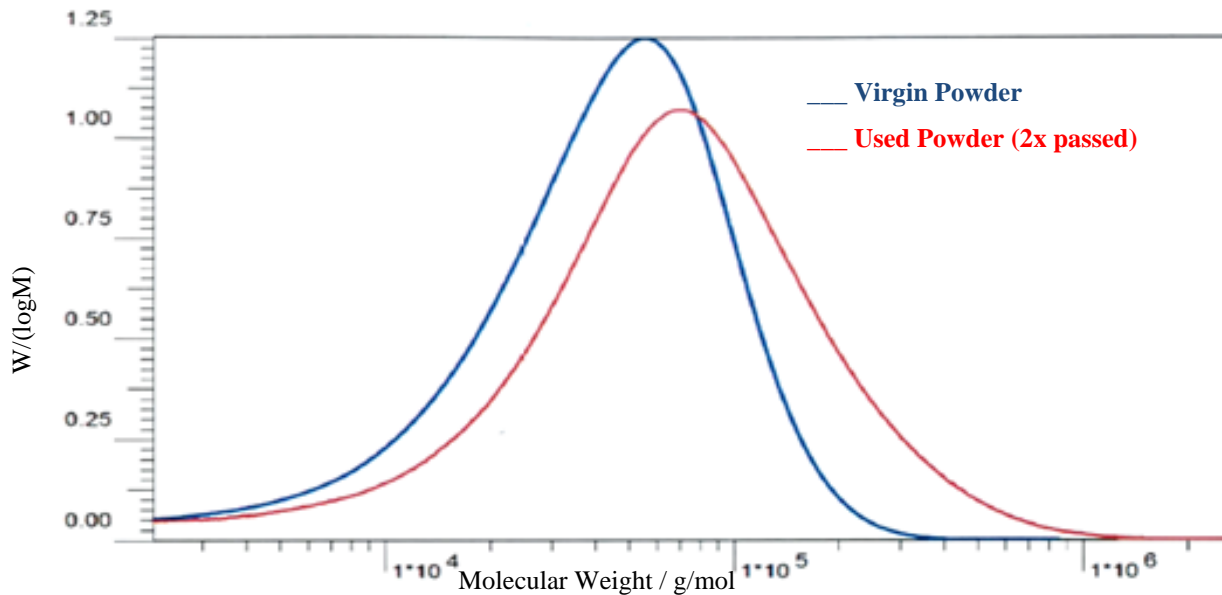


Figure 3: molecular weight distribution from SEC-analysis [DMRC12]

Even though the viscosity of the melted plastic has a strong influence on the quality of the product, only few examinations have been conducted in the field of rheology. Using melt curves the viscosity of the melt can be displayed by means of different shear rates. Some melt curves have been determined using high pressure capillary viscometers. The melt curves have to be seen very critical, since there is almost no process related shearing during the LS process and high pressure capillary viscometers cannot operate at small shear rates. The department of materials of the University of Loughborough has thus determined melt curves with a rotation rheometer, since this method allows the measurement of very small shear rates. However only melt curves of new and old powder have been compared to each other, in which case the differences were traced back to the post polymerization in the material [Haworth11].

The rapid prototyping center of the University of Louisville has examined the change of the mechanical properties elongation at break and tensile strength with differently aged powders. Here the part cake and the powder from the overflow container from the first build job were homogenized again and used for the next build job. This process was repeated several times. The results are displayed in figure 4 [Gornet02]. It can be seen that the elongation at break already increases for the second build job (from ~2200 PSI up to ~3600 PSI), while the tensile strength stays constant and only decreases after the fifth build job. These results, given in Figure 4, illustrate that through the mixing of virgin and old powder mechanical properties about ~3600 PSI can be achieved, which is about 63% higher than for virgin powder [Gornet02].

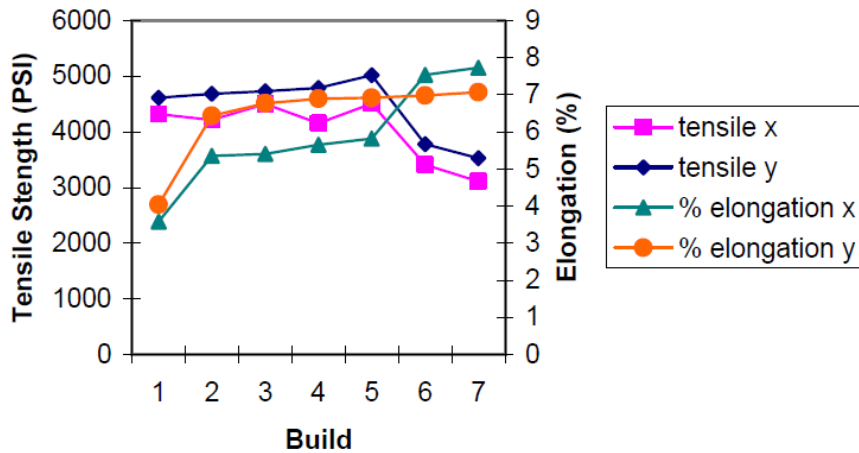


Figure 4: change of the mechanical properties tensile strength and elongation [Gornet02]

The comparison of all the previous results shows that the change of properties of the powder can be traced back to a post polymerization respectively networking of the molecules, characterized by various methods. These results are unexpected with regards to the standardized injection molding process, since examinations of the structural change of plastics during injection molding show a chain reduction. But what is missing for nearly all examinations is a reference to the properties and the quality of parts that were manufactured with aged powder. The objective has to be to follow up on the present results and methods, so that they can be used as a receiving respectively quality control, in order to be able to characterize the quality of the final products.

#### 4 Basics

##### *Melt Volume Rate*

The basic rheological characteristic values can be described easily using the two plate model.

The two plate model shall reflect the load situation that a plastic is exposed to during processing. One condition is that the plastic is adhesive at both plates and that laminar flow connections dominate. The upper plate is moved with the shear force  $F$  against the lower plate. The lower plate is fixed, thus has a speed of  $v=0$ . The plastic in between both plates is being deformed and subjected to a shear load. The force  $F$  over the height  $h$  causes a shear stress, which is defined as follows:

$$\tau = \frac{F}{A} \tag{1}$$

Since the upper plate is moved with the force  $F$  and the lower plate is fixed, a velocity profile as shown in the figure below is set. The resulting liquid layers are displaced contrary to each other.

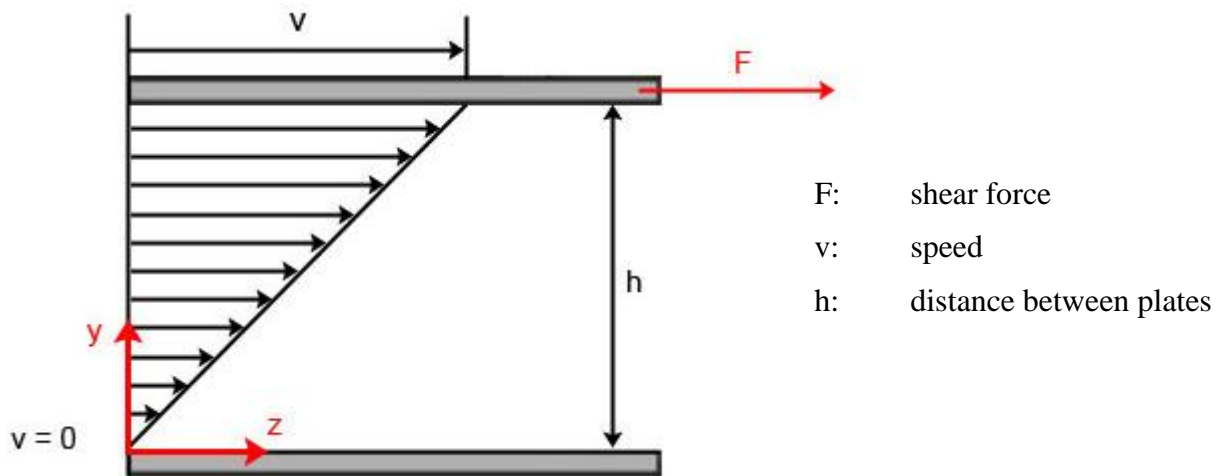


Figure 5: Velocity profile in the two plate model

The effective shear stress deforms each individual liquid layer with a specific shear velocity. The shear velocity is also known as shear rate and is defined as follows:

$$\dot{\gamma} = \frac{\partial v}{\partial y} = \frac{v}{h} \quad (2)$$

The ratio between shear stress and shear velocity is a material constant for an ideal viscous fluid at a constant temperature. This proportionality factor is called viscosity and is a material related value.

$$\eta = \tau / \dot{\gamma} \quad (3)$$

The viscosity is a material factor for the flow rate of a material. When flowing, the molecules of a material are displaced against to each other. The inner resistance against the friction can be described as the viscosity [PahlL95] [RH10] [Schoe11].

### *Solution Viscosity*

With a low pressure capillary viscometer the viscosity of a laminar flowing fluid can be determined according to DIN EN ISO 1624. The basis for the measurement of the viscosity is the law according to *Hagen-Poiseuille* [1624].

$$\eta = \frac{\pi \cdot r^4 \cdot g \cdot h \cdot \rho \cdot t}{8 \cdot l \cdot V} = A \cdot \rho \cdot t \quad (4)$$

Nomenclature:  $r$  = radius of the capillary,  $g$  = force of gravity,  $h$  = height of the flowing fluid,  $\rho$  = density of the fluid,  $\frac{V}{t}$  = liquid volume, which flows through the capillary per time unit,  $l$  = length of the capillary

In order to characterize polymers using the solution viscosity, they are dissolved in a solvent. The actual measurement is a comparison measurement of the polymer solution and the pure solvent. For this purpose the relative viscosity is defined by the quotient from the viscosity of the polymer solution to the viscosity of the solvent. All factors that refer to the pure solvent are marked with a  $0$  in the index [MC05].

$$\eta_{rel} = \frac{\eta}{\eta_0} = \frac{\rho t}{\rho_0 \cdot t_0} \quad (5)$$

In order to be able to better show the change of the viscosity, the specific viscosity is defined.

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \eta_{rel} - 1 \quad (6)$$

From  $\eta_{sp}$  the reduced viscosity respectively the viscosity number  $\frac{\eta_{sp}}{c}$  can be determined; whose limiting value for smaller concentrations is the intrinsic viscosity respectively the boundary viscosity [PC96].

$$\eta = \lim_{c \rightarrow 0} \frac{\eta_{sp}}{c} = \lim_{c \rightarrow 0} \frac{\eta - \eta_0}{\eta_0 c} \quad (7)$$

For diluted solvents, which have a concentration  $c$  of less than 10g per liter, the densities of the polymer solutions and the solvent are nearly identical. For that reason the density is canceled from all the above formulas, so that the boundary viscosity can be determined via the time measurement [MC05].

$$\eta = \lim_{c \rightarrow 0} \frac{\eta - \eta_0}{\eta_0 c} \approx \lim_{c \rightarrow 0} \frac{t - t_0}{t_0 c} \quad (8)$$

The determination of the boundary viscosity is done with a graphic method, with which the boundary viscosity can be extrapolated over a linearization. The following formulas are possible:

$$\eta_{red} = \eta + k_H \eta^2 \cdot c \quad (9)$$

$$\eta_{red} = \eta + k_{SB} \cdot \eta \cdot \eta_{sp} \quad (10)$$

Formula (9) shows the plotting according to *Huggins* and formula (10) according to *Schulz-Blaschke* [PC96].

#### *Exposure strategy - Part Property Profiles developed by EOS Company*

EOS Company offers standardized exposure parameters for all types of laser sintering machines. The aim of this standardization is the determination of resilient values for material properties [INT1]. By using the same parameters and running the same systems reproducible properties shall be possible. This work is performing material tests using an EOSINT P395 laser sintering machine. All kind of material properties like mechanical, thermal, electrical and physical properties are considered. Further on it is possible to test these properties by using self-created exposure strategies which is possible using the Developer Kit. In this work the pretests using a layer thickness of 120µm and the EOS Part Property Profiles for this layer thickness are shown.

As an exposure strategy the following EOS Part Property Profiles are used in this work [INT1]:

Parameter	Layer Thickness / µm	Temperature /°C	Recoater blade geometry
Top Speed	180	181	Triangle
Speed	150	180	Triangle
Balance	120	179	Round

Performance	100	178	Round
Top Quality	60	177	Flat
Developers Kit	Personalized Parameter		

Table 1: exposure strategy by EOS Part Property Profiles [INT1]

## 5 Experimental Setup

### *Building Job*

A building job has been designed in order to get information about mechanical properties of laser sintered parts. Four warpage plates at the bottom are placed to get information about the warping and shrinkage. These test specimens have two advantages: on the one hand the warpage as well as the shrinkage of laser sintered parts can be determined. On the other hand these plates have a huge surface area and therefore it should be possible to see sink marks, which are dependent on the powder quality, e.g. the powder ageing. Further on a 5x5 matrix with tensile bars placed in z- direction is built on top of the warpage plates. The z-direction is chosen because it is the weakest direction in laser sintering [RUES11]. For testing the mechanical properties the nine central placed test specimens are used to create the average value. At that position the assumption of a homogenous building area can be accepted.

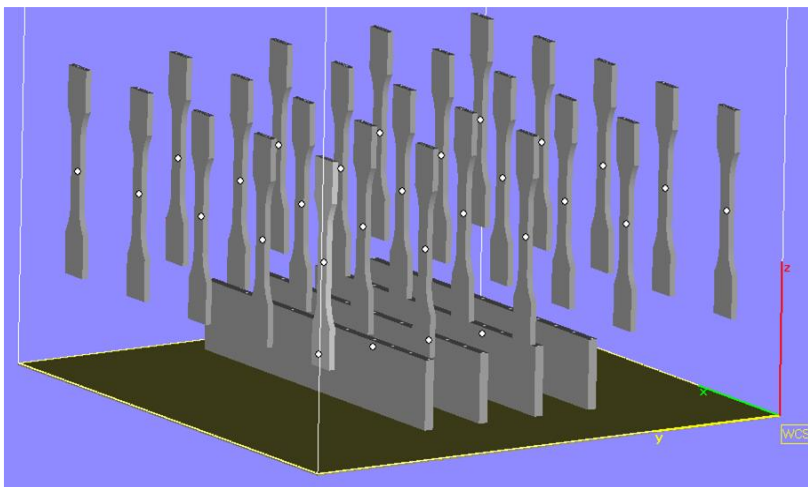


Figure 6: Test job to determine powder quality as a function of mechanical properties

The test specimens are placed in x-direction to avoid big edges along the recoater and to reduce the probability of any job terminations.



### Material Ageing

The tests during this work were performed by using nylon 12 cycle-powders (PA2200) from one batch. The powder age is known, so for the 1<sup>st</sup> experiments a powder ratio of virgin powder and used powder is used with the amounts adjusted by controlling the MVR (see figure 7).

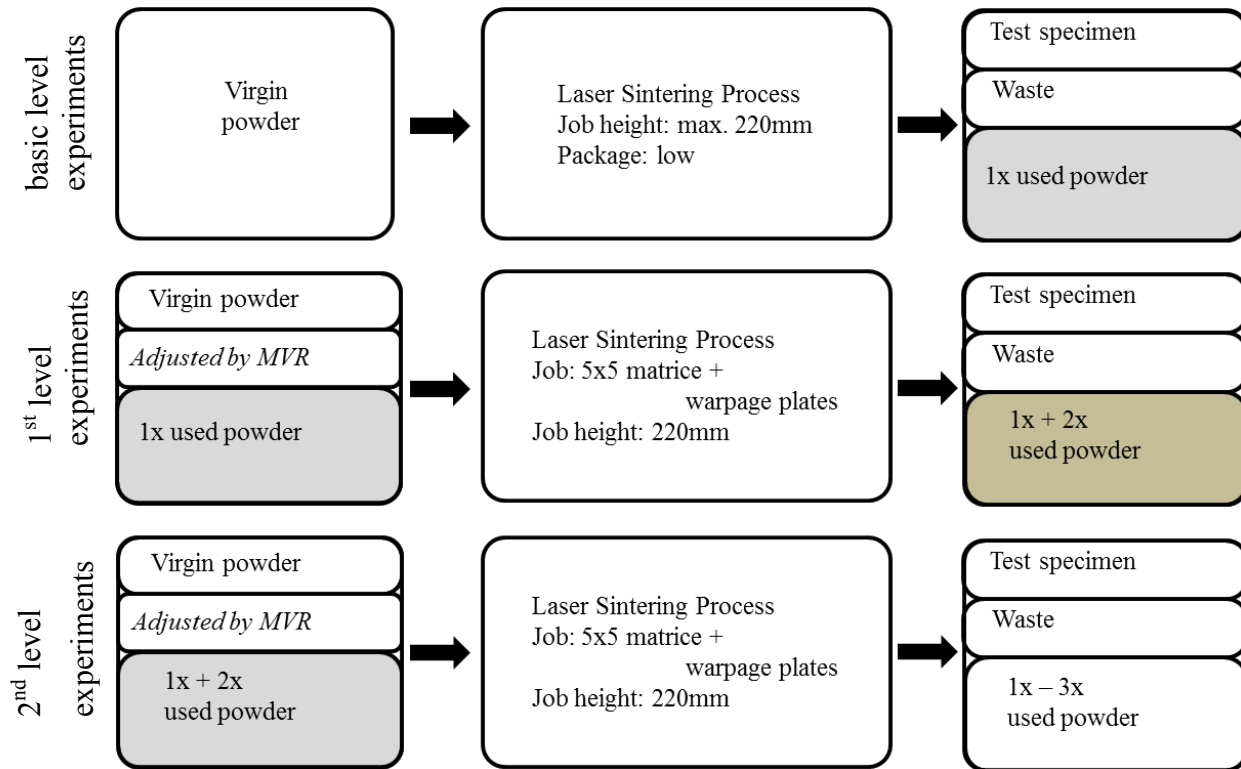


Figure 7: Powder usage for laser sintering process

The used powder is taken from first tests at the DMRC performed by using only virgin powder, so it is known that the used powder has run one time through the laser sintering machine: a onetime thermally charged powder (1x used powder) with a good quality is used. For the MVR 2<sup>nd</sup> experiments this powder is homogenized and mixed with a virgin powder again: a one-two time thermally charged powder (1x+2x used powder) is used in this case.

### Sample preparation for MVR measurement

The material investigated in this work is prepared by using a standard concrete mixer. The mixing procedure takes 10 minutes clockwise and 10 minutes anticlockwise.

As a preparation for the measurement of the MVR value it has to be ensured that no segregation of the powder has taken place in the current storage form for the nylon 12. Since this inevitably happens it is recommended to split the powder using a Retsch spinning sample divider. Eight circularly mounted glass containers are attached a rotating device. The powder is continuously fed and thus homogeneously distributed among the eight containers.

For using the test sample in an MVR measurement device it is important to dry the material. The DMRC drying process is performed by using a Thermo scientific furnace. The sample is heated up to 105°C for 10 minutes. The temperature is further risen up at 140°C for another 2 minutes whereas the rising up procedure takes another 5 minutes. After the preheating process the sample

is given to the melt volume rate measurement device. To guarantee a high reproducibility and to guarantee a dry sample (no moisture adsorption on the way from the preheating process to the MVR measurement device) this procedure is treated within a time interval of 20...30 seconds. The temperatures are similar to the EOS drying process, but they are using a *Sartorius MA100* moisture balance. EOS Company is realizing a rising up time from 105°C up to 140°C which is about one minute. [EOS11]

#### *Sample preparation for Solution Viscosity Measurement*

Previous to each measurement a stock solution with a concentration of 10g/L was prepared. Each series of measurements consists apart from the stock solution of four additional solutions, whose concentrations were set by diluting the stock solution. The set concentrations were 1g/L, 2 g/L, 4 g/L und 6 g/L. With the weight balance *AT261 Delta Ranger* from the company Mettler 500±0,1 mg were placed in a 50ml Erlenmeyer flask, with an accuracy of one tenth of a milligram.

Afterwards 50±0,1 ml were pipetted into the Erlenmeyer flask. During the pipetting it is important to take a reading in the lower half of the meniscus.

The closed Erlenmeyer flask is placed in an ultrasound basis for 60 minutes at 30°C in order to accelerate the preparation of the solution. It is important that the temperature in the ultrasound basis doesn't increase above the glass transition temperature of the nylon 12 (ca. 45°C), since otherwise the chain structure could be influenced before the measurement. Afterwards the stock solution is stored at room temperature for 24 hours, since only after this time the nylon 12 will be completely dissolved.

#### *Conditioning and cooling down phase*

The test specimen are tested in a dry condition, which means that the samples are vacuumed after the post process to reduce any influence of the environment, and at nearly standard atmosphere ( $T_R=22^\circ\text{C} \pm 1^\circ\text{C}$  and  $rH=50\% \pm 10\%$ ). It is possible to investigate different cooling down phases and their influence on mechanical properties. All test specimens are tested dry. Directly after finishing the LS process the building chamber remains 10 hours within inert gas atmosphere within the LS machine. After this time the test specimens are unpacked immediately, respectively after duration of another 24 hours. All test specimens are vacuumed to perform tests with same conditioned samples.

## **6 Applied Testing Methods**

### *Tensile Testing - Mechanical investigation*

Because there is no adequate standard for tensile bars manufactured by Laser Sinter processing, the test method standard is based on the injection molding standard DIN EN ISO 527-1 till DIN EN ISO 527-5. The test speed was 1mm/min to get information about the Young's modulus and 50mm/min to get information about the tensile strength and the elongation at break. The velocities are given in the usual polyamide standard DIN EN ISO 1874 [527-1-5] [1874].

### *Melt Volume Rate*

The Melt Volume Rate (MVR) is used for simple quality control and to be able define the volume flow characteristics of polymer melts during processing. The device used to determine the MVR is a low-pressure capillary viscometer. It stands out because the power of the piston is generated using its weight. Thus the device from this test is a pressure operated viscometer. In this work a Zwick/Roell “mflow” measurement device is used for DMRC measurement [RH10]. The melt volume rate measurement is performing by using the following parameter:

Test parameter for EOS and DMRC	Virgin & Used powder
Nominal load	5 kg
Sample quantity	4,0 g
Preheating time	300 s
Temperature	235 °C
Piston distance	14,6 mm

Table 2: Parameter for MVR measurement

These parameters are the same for the testing with DMRC equipment as well as with EOS equipment. As a result a comparison between EOS measurement and DMRC measurement is given as well. The EOS measurement is performed by using a *MeltFlow @on* by Karg Company [INT1].

#### *Solution Viscosity*

After the complete dissolving of the material the stock solution is filtered, in order to ensure that no solid particles remain in the solution, which could possibly clog the capillaries. According to DIN EN ISO 307 a glass filter with the porosity 2 and a pore width of 40-100  $\mu\text{m}$  is used. In order to clean the filter it is flushed under pressure with methanol several times from both sides. Methanol is a good cleaning agent since in it the m-Cresol dissolves. All used vessels are cleaned several times with methanol after their use and left in the vent until the methanol has completely evaporated [307].

For different measurements with different concentrations the following concentrations are created:

Concentration / g/L	Concentration / g/mL	Solid material in 20 ml / g	Amount of stock solution / ml	Amount of solvent / ml
10	0.01			
6	0.006	0.12	12	8
4	0.004	0.08	8	12
2	0.002	0.04	4	16
1	0.001	0.02	2	18

Table 3: Mixture for concentration of the measurement points

With the different concentrations it is possible to plot a curve for the solution viscosity and to detect the intrinsic viscosity as well as the viscosity number.

## 7 Results

### *Melt Volume Rate*

Table 4 shows the results for the melt volume rate measurement. The left column is showing the MVR number. In this context the value MVR0 means homogenized used powder, which has one through the laser sintering machine (1x used powder) one time. The value MVR6 is showing the results for 100% virgin powder from one batch. The values MVR1...MVR5 are obtained for different powder qualities adjusted by using the MVR measurement. The columns *MVR Value EOS* and *MVR Value DMRC* are showing the results for the DMRC and the EOS measurement processes, respectively. It can be clearly recognized that the absolute values are different between the processes. The reasons for the differences are the different MVR measurement devices as well as the different preheating processes by using different preheating devices. However, the deviation between EOS and DMRC measurement are similar and almost constant with the MVR values for the DMRC measurement being 4.5-5.5cm<sup>3</sup>/10min higher than the respective values obtained by EOS Company. Further investigations will be performed to evaluate the differences by using different devices.

MVR#	1 <sup>st</sup> level experiments						2 <sup>nd</sup> level experiments (Add On)				
	Virgin Powder	MVR Value EOS	MVR Value DMRC	Standard Deviation	Relative Deviation	Viscosity	Virgin Powder	MVR Value DMRC	Standard Deviation	Relative Deviation	Viscosity
	%	cm <sup>3</sup> /10m in	cm <sup>3</sup> /10m in	cm <sup>3</sup> /10m in	%	Pa · s	%	cm <sup>3</sup> /10m in	cm <sup>3</sup> /10m in	%	Pa · s
0	0	N/A	N/A	N/A	N/A	N/A	0.00	22.81	0.63	2.74	20.11
1	7	20	25.59	0.44	1.72	17.93	10.70	24.85	0.8	3.21	18.46
2	18	24	28.48	0.48	1.69	16.11	20.31	27.60	0.98	3.56	16.62
3	26	28	31.27	1.02	3.25	14.67	24.40	30.81	0.85	2.75	14.89
4	39	32	36.20	0.76	2.11	12.67	46.80	35.94	0.35	0.97	12.76
5	50	36	40.04	0.84	2.09	11.46	52.90	42.00	1.28	3.08	10.92
6	100	N/A	68.29	0.74	1.12	6.72	100.00	68.29	0.74	1.12	6.72

Table 4: MVR measurement

The columns *Standard Deviation* as well as *Relative Deviation* are showing the results for the DMRC MVR measurement method. The MVR value for the MVR6 measurement is given as an average value of 20 individual measurements to get information about the resilience. The other values are obtained as an average from 5 individual measurements. The values are showing a huge reproducibility within a small significant range.

In the right side of table 4 (2<sup>nd</sup> level experiments) the MVR values for the 2-pass powder experiments are given, using differently aged powder as explained above. It is shown that we could obtain mixtures with similar MVR values for both types of used powders. Further on the viscosity is determined by using the formulas presented above.

In the next figure the reproducibility of the melt volume rate measurement is shown. A quadratic curve characterizes the powder quality for regarding different melt volume rates. The MVR are represented for 1<sup>st</sup> level (MVR\_1x-passed) and 2<sup>nd</sup> level (MVR\_2x-passed) powder qualities.

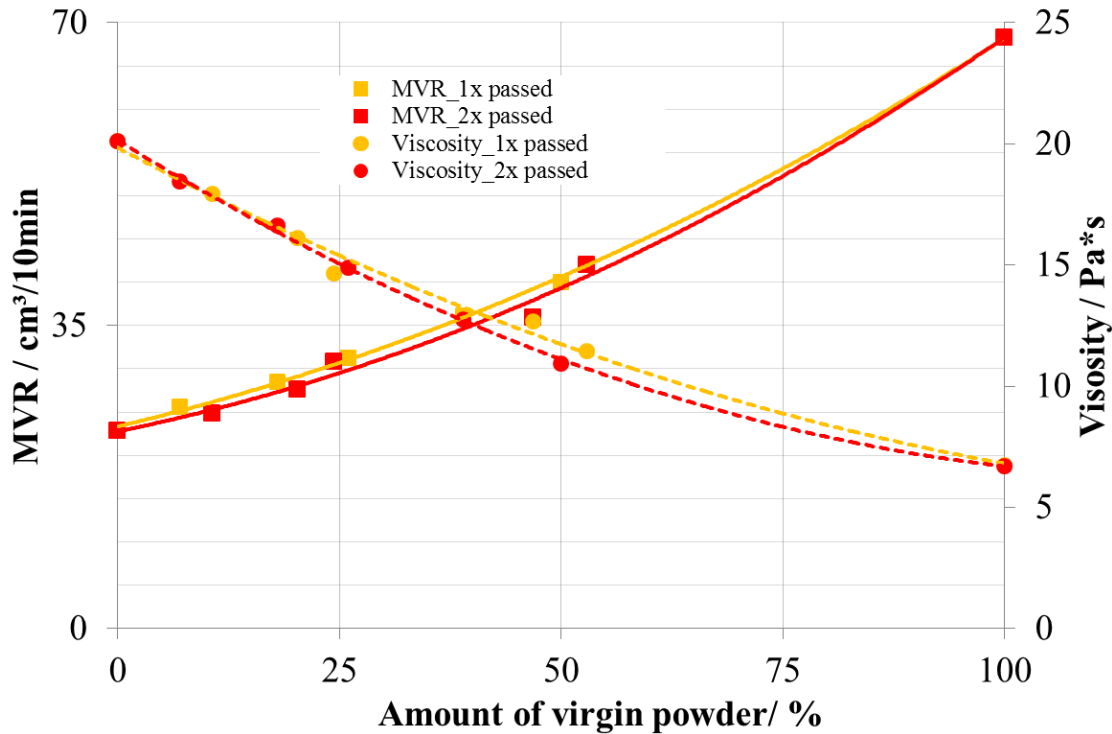


Figure 8: MVR measurement – reproducibility

The quadratic curve is almost coinciding for both measurements. The measurements are performed with a high reproducibility and all values are reproducible with a deviation about  $\pm 2\%$ . However, the MVR measurement is a simplifying method to get information about the viscosity. The viscosity behaves inversely which is represented for the curves Viscosity\_1x-passed and Viscosity\_2x-passed. The lower the melt volume rate is the higher is the powder melt viscosity. The lower the amount of virgin powder is the higher is the viscosity.

Unfortunately, the MVR gives only one value at the flow curve. Besides conventional methods as capillary rheometry or rotational rheometry (Haworth, Hopkinson, Hitt and Vasquez are showing differences by using virgin and used powder regarding both methods [HHHV11]), a reasonable approach to polymer properties is the detection of the solution viscosity. The next figure shows the solution viscosity with respect to polymer concentration using m-cresol as solvent (nylon 12 is soluble in m-Cresol). Different linear curves are given for chosen sample compositions. The curve is extrapolated to the y-axis where the intrinsic viscosity is given. Another regarded parameter is the viscosity number at a concentration of 10g/L. It is noticeable, that the viscosity is higher, the lower the amount of virgin powder. Further on the differences regarding the intrinsic viscosity aren't as high as regarding the viscosity number for concentrations (amount of powder/amount of solution) about  $c=1\text{g/cl}$  up to  $c=10\text{g/cl}$ .

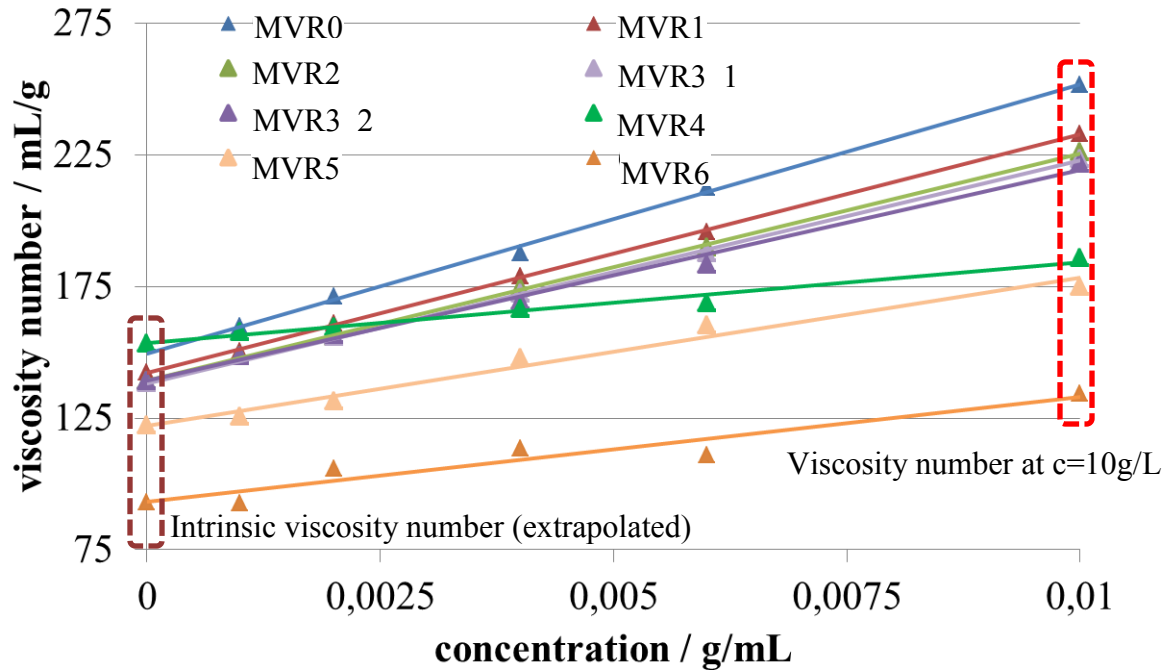


Figure 9: Solution Viscosity measurement

Regarding the single values the discussions above are apparent. Using a sample of used powder (intrinsic viscosity = 149.62 mL/g), the intrinsic viscosity is much higher than with a powder sample of virgin powder (intrinsic viscosity number = 93.17 mL/g) and all values are within a range of about 60 mL/g. Regarding the viscosity number at a concentration of 10g/l all values are within an range of 110 mL/g.

Furthermore it is important to observe the curve slope: The higher the slope, the higher the amount of used powder by using the same powder quality. Regarding the virgin powder it is noticeable, that this slope is the lowest one of all observed samples, except the curve for MVR4. Because of not having enough powder for the performing of two jobs, there is 2-3kg of several times used powder, taken from the DMRC cycle powder, within the powder mixture for MVR4. This powder is running through the laser sintering process much more than 2 times, so the used powder is much older than the used powder usually used in this work. It is important to know, because of the low slope for that curve. It seems to have a huge influence on the curve and on the viscosity number as well as a smaller, but visible influence on the intrinsic viscosity number. Because of these results the solution viscosity, the viscosity number and the slope (slope = 3.23, much smaller than all other slopes) seem to be a really sensitive method to detect changes of the powder quality. Further on the reproducibility regarding the solution viscosity is tested. The powder quality MVR3 is tested two times (3\_1 and 3\_2 and it is shown, that there aren't any significant deviations between the two measurements. The measurements are reproducible within a range about 0.6% (for the intrinsic viscosity number) up to 1.0% (for the viscosity number at a concentration of c=10g/L).

#	0g/L	c=1g/L	c=2g/L	c=4g/L	c=6g/L	c=10g/L	slope
	0	0.001	0.002	0.004	0.006	0.01	
	intrinsic viscosity number (extrapolated on y-axis)	g/mL	g/mL	g/mL	g/mL	g/mL	-
0	149.62	105.06	133.84	176.77	159.16	241.98	9.24
1	142.40	150.29	160.94	179.08	195.69	232.89	9.05
2	139.24	148.51	155.83	174.63	189.81	226.15	8.69
3_1	138.27	72.08	155.79	172.35	187.53	223.62	8.53
3_2	139.15	148.70	156.55	169.35	183.47	221.59	8.24
4	153.52	157.68	159.47	166.64	168.78	185.85	3.23
5	122.62	125.58	131.38	147.93	160.27	174.96	5.23
6	93.17	92.63	106.00	113.46	111.00	134.37	4.12

Table 5: Viscosity number at different concentrations and intrinsic viscosity number (extrapolated at c=0g/L)

The next step of this work is the correlation of the MVR value, and therefore of the solution viscosity, regarding mechanical properties. Further on the influence of different cooling down phases are investigated as well. The next diagram is showing the tensile strength for accomplished tensile tests using the test job explained in figure 5. The primary y-axis shows the tensile strength in MPa or the Elongation at break in %, respectively, the secondary axis gives the melt volume rate. The sample nomenclature on the abscissa denotes the adjusted MVR value (see Table 4) by the first number. The second number denotes the amount of repetitions.

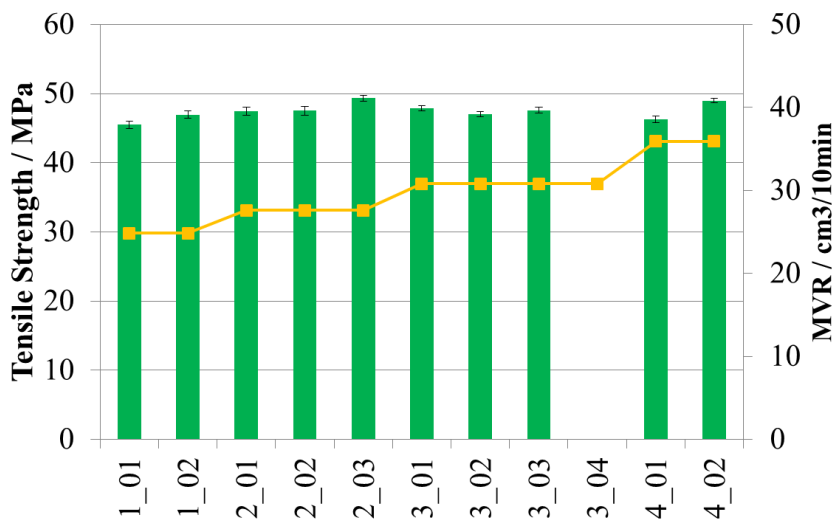


Figure 10: Tensile strength as a function of powder with different MVR values and a cooling down phase of 10h



For the tensile strength after a cooling down phase of 10 hours it is difficult to find significant deviations. There are differences regarding the results for the MVR1-powder quality and the other results. The tensile strength for 2\_03 seems to be the highest value which differs from the other results for 2\_01 and 2\_02. For the MVR3 values the results are reproducible and the total results are similar to the other results obtained from different powder qualities.

The results for the tensile strength after a cooling down phase of 10 hours + 24 hours are similar. Further on there seem to be differences between the different powder qualities. The MVR3 powder seems to have the highest absolute values. This was reproduced for the other values.

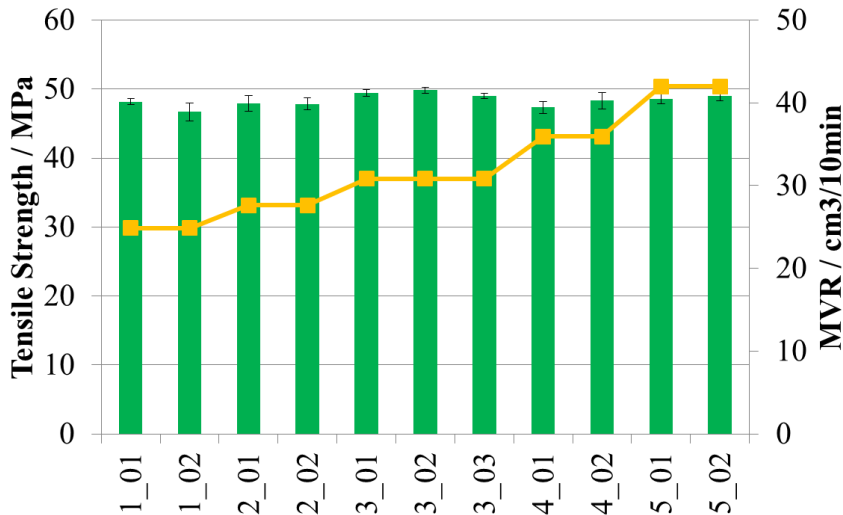


Figure 11: Tensile strength as a function of powder with different MVR values and a cooling down phase of 10h+24h

The absolute values are slightly higher than values after a shortened cooling down phase. This behavior is due to the laser sinter material. Semi crystalline thermoplastics are composed of crystalline and amorphous regions. The unpacking temperature using a 10 hour + 24 hour cooling down time is about 50°C. The unpacking temperature for the experiments using a 10 hour cooling down phase is about 120°C and therefore much higher than the glass transition temperature, which is about 45°C. That implies that the crystallization process of the material structure is not finished. The part will be quenched and the crystallization level as well as the crystallization structure depends significantly on the cooling down process. A faster cooling down phase prefers smaller crystalline regions and, therefore, a smaller crystallization level, a smaller crystallinity. However, decreasing the crystallinity means the reduction of tensile strength, but an increase of the elongation at break. This phenomenon is visible in the diagrams showing the tensile strength as well as the elongation at break [SCHOE11].

The values for the elongation at break are high for test specimens placed in z-direction. The elongation at break for some test specimens is rising up to 20%. But it is visible that this is not reproducible. There are significant deviations although the test specimens are built up using the same exposure parameters and the same powder quality. The reason is the unpacking procedures. Depending on the person it is possible that different unpacking behaviors have an influence on the crystalline regions. However, it is possible to get results about 47MPa±2 for the elongation at break in z-direction, but the reproducibility is not given.

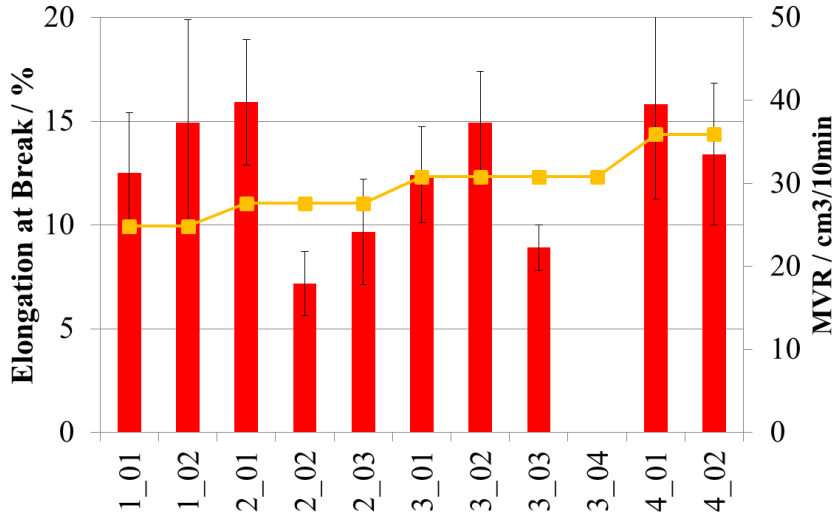


Figure 12: Elongation at break as a function of powder with different MVR values and a cooling down phase of 10h

The elongation at break for a cooling down phase of *10 hours + 24 hours* shows a different behavior. The absolute values are smaller than after a cooling down phase of only *10 hours*, but the reproducibility is shown. Further on the elongation at break is rising up together with the different MVR powder qualities and therefore with the amount of new powder. This phenomenon is visible for the first three values. For the MVR4 and MVR5 powder it seems to be a decrease. One possible explanation might be the quality of the used powder, which has a good quality (maximum times of passing the laser sintering process: 2x). Similar tests shall be performed for typical cycle-powder to find a correlation about similar powder qualities adjusted by the MVR value, but as a mixture of different aged used powder.

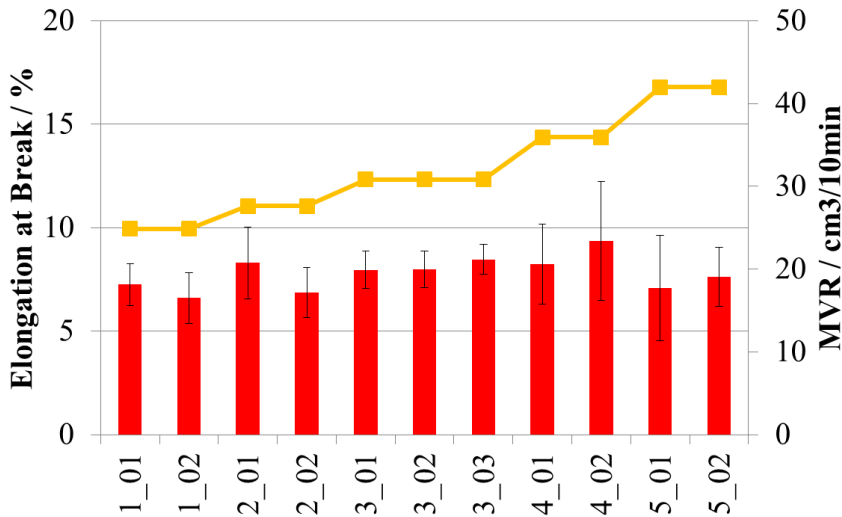


Figure 13: Elongation at break as a function of powder with different MVR values and a cooling down phase of 10h+24h

One noticeable result not reflected in mechanical strength is the surface quality of laser sintered parts. The surface looks really bad using a powder quality with a small amount of virgin powder like the powder mixtures MVR1 and MVR2. Most of the test specimens, placed within the

corners of the building platform, are looking similar. An extract figure (figure below) shows a tensile test specimen.



Figure 14: deformed tensile test specimen built with a powder quality MVR1 or MVR2, placed in a corner of the building platform.

After these results there is an influence of different powder qualities on the mechanical properties that can be seen. It might be possible that the mechanical properties are robust toward different powder qualities using the melt volume rate as well as the solution viscosity as a quality criterion, but there are differences regarding the surface quality as well.

## **8 Summary and Outlook**

The results are showing a possible way to measure the rheological properties of nylon 12 powders. It is possible to get reproducible values using the MVR method. Further on the thermal ageing has a huge influence on the viscosity. The higher the amount of used powder, the lower is the melt volume rate, the higher is the viscosity. Similar statements can be made regarding the solution viscosity. It is possible to reproduce solution viscosity results within a small significant deviation. Further on the intrinsic viscosity as well as the viscosity numbers are showing distinct differences with respect to powder mixture ratio regarding the ageing of used powder. Besides the slope of the solution viscosity seems to be an important parameter as well. Depending on the age of the used powder it is possible to get a powder mixture with the same melt volume rate but with different slopes for the solution viscosity. The mechanical properties seem to be robust by investigating different powder qualities. In some cases there are small deviations regarding tensile strength as well as elongation at break, but there are more tests needed. Further on there is a huge influence on the surface quality. Mechanical properties and surface quality have to be considered simultaneously because there will be a correlation between the above mentioned properties and the powder quality and the usage of different aged used powder. Another criterion is the quality of the used powder, which might be unusually high in the experiments presented here. Another experiment to do would be the usage of a heavily used nylon 12 material mixed with virgin one.

Further on it is noticeable that the unpacking behaviors as well as the cooling down phase have a very severe impact on the mechanical properties. The results are reproducible using a longer cooling down phase. It is important to know the unpacking temperature and to avoid a too fast cooling down phase.

After all it is important to know the complete laser sintering quality chain, because lots of the different steps have different influence on the final quality of laser sintered parts. The next steps include a quality job with test specimen to test different characteristics like thermal, electrical and physical properties, as well as the linear and elastic mechanical properties. The influence of different powder ageing shall be tested as well.

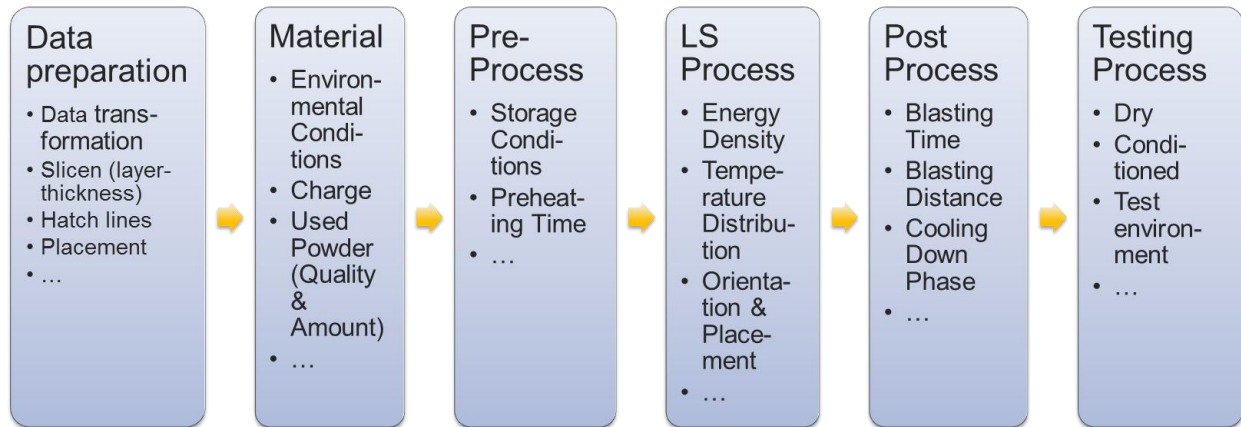


Figure 15: Laser Sintering Quality Process Chain

All properties shall be investigated by using all available layer thicknesses. Therefore all known influencing factors have to be considered, starting with the data preparation. It is important to know the number and position of hatch, edge and contour lines and the shrinkage has to be taken into consideration as well. Pretests already gave valuable information about the dependence on placement, orientation and positioning, thereby it is possible to reduce the amount of test specimen within the quality job. The powder mixtures of virgin powder with differently aged recycled material, adjusted by equal melt volume rates, will be investigated as well. Further on there will be lots of other rheological investigations to get information about a sensible way to characterize the quality of starting material, because for laser sintering as a serial production method it is tremendously important to reliably characterize the input material. Next to usual nylon 12 material another, at the moment not mentioned material, will be tested. The pre-process, including storage conditions and preheating time, will be kept constant for the duration of the test phase. By investigating the influence of different layer thicknesses, the EOS part property profiles shall be used as well as own developed exposure strategies. An automatic blasting system will be installed in order to reduce the influence of the blasting post process. The cooling down phase will be constant at 10 hours within the laser sintering machine and another 24 hours at standard atmosphere. Further on the conditioning of nylon 12 parts will be defined as well as the test environments and the individually testing methods.

## 8 Reference

- [1624] DIN EN ISO 1624: Kunststoffe - Vinylchlorid-Homo- und Copolymerisate - Siebanalyse im Wasser (ISO 1624:2001); Deutsche Fassung EN ISO 1624:2001; June 2002
- [1874] DIN EN ISO 1874: Kunststoffe - Polyamid (PA)-Formmassen - Teil 1: Bezeichnung (ISO 1874-1:1992); Deutsche Fassung EN ISO 1874-1:2000; February 2002
- [ 307] DIN EN ISO 307 Kunststoffe - Polyamide - Bestimmung der Viskositätszahl (ISO 307:2003); Deutsche Fassung EN ISO 307:2003; December 2003
- [527-1-2] DIN EN ISO 527-1: Kunststoffe - Bestimmung der Zugeigenschaften - Teil 2: Prüfbedingungen für Form- und Extrusionsmassen (ISO 527-2:2012); Deutsche Fassung EN ISO 527-2:2012; June 2006

- [DMRC12] S. Ruesenberg, H.-J. Schmid: Determination of Material Properties by references to a Real Product, optimized for Laser Sintering - SEC measurement of laser sintering powder.
- [Drummer10] D. Drummer; F. Kühnlein; D. Rietzel; G. Hülde: Untersuchung der Materialalterung bei pulverbasierten Schichtbauverfahren. RTejournal, 2010
- [EOS11] H. Pfisterer: Application method for melt volume rate measurement. EOS Company, Munich, Germany, June 2011
- [Gornet02] T.J. Gornet; K.R. Davis; T.L. Starr; K.M. Mulloy : Characterization of Selective Laser Sintering<sup>TM</sup> Materials to determine Process Stability. Rapid Prototyping Center, J.B. Speed Engineering School. University of Louisville, Vogt Building. Room 101. Louisville. KY 40292
- [HHHV11] B. Haworth Barry; N. Hopkinson; D. Hitt; M. Vasquez: Influence of Molecular Weight and Viscosity on Particle Coalescence for Laser Sintering of Nylon-12. Conference: Polymer Processing Society - Marrakesh, Morocco - May 2011
- [INT1] EOS  
[http://www.eos.info/fileadmin/user\\_upload/downloads\\_presse/pdf\\_files/EOS\\_WP\\_PPP\\_d.pdf](http://www.eos.info/fileadmin/user_upload/downloads_presse/pdf_files/EOS_WP_PPP_d.pdf)
- [INT2] <http://www.chemie.tu-dortmund.de/fb03/de/Studium/Praktika/PC/Ablage-PDF/Rheologie.pdf>
- [MC05] B. Tiede: Makromolekulare Chemie Eine Einführung. 2 überarbeitete Auflage, Wiley-VCH Verlag, Weinheim 2005
- [Pahl95] M. Pahl; W. Gleißle; H.M. Laun: Praktische Rheologie der Kunststoffe und Elastomere. VDI-Verlag GmbH, Düsseldorf 1995
- [PC96] K.-F. Arndt; G. Müller: Polymer Charakterisierung. Carl Hanser Verlag, München, 1996
- [PDY08] D.T. Pham; K.D. Dotchev; W.A.Y. Yusoff: Deterioration of polyamide powder properties in the laser sintering process. Part C: Journal of Mechanical Engineering Science 2008
- [RH10] T.G. Mezger: Das Rheologie Handbuch: Für Anwender von Rotations- und Oszillations-Rheometern. 3. Überarbeitete Auflage, Vincentz Network, Hannover 2010
- [Rues11] S. Ruesenberg, H.-J. Schmid: Mechanical Properties as a result of multitude of parameters; European Forum on Rapid Prototyping – Rapid Prototyping and Manufacturing; France, Paris, June, 12<sup>th</sup>-14<sup>th</sup> 2012
- [Schoe11] V. Schöppner, Skript: Grundlagen der Kunststoffverarbeitung. Kunststofftechnik KTP, Universität Paderborn, Paderborn, Germany, 2010
- [ZHKV06] H. Zarringhalam, N. Hopkinson, N.F. Kamperman, J.J. de Vlioger : Effects of processing on microstructure and properties of SLS Nylon 12. Materials Science and Engineering A 435–436 (2006)