

# MATERIAL PROPERTIES OF LASER SINTERED POLYAMIDE 12 AS FUNCTION OF BUILD CYCLES USING LOW REFRESH RATES

Stefan Josupeit<sup>1</sup>, Johannes Lohn<sup>1,2</sup>, Eduard Hermann<sup>2</sup>, Monika Gessler<sup>3</sup>, Stephan Tenbrink<sup>3</sup> and Hans-Joachim Schmid<sup>1</sup>

<sup>1</sup>Direct Manufacturing Research Center (DMRC) and Particle Technology Group (PVT),  
University of Paderborn, Germany

<sup>2</sup>Phoenix Contact Deutschland GmbH, Blomberg, Germany

<sup>3</sup>EOS Electro Optical Systems GmbH, Krailling, Germany

Contact: [stefan.josupeit@dmrc.de](mailto:stefan.josupeit@dmrc.de)

REVIEWED

## Abstract

Due to long process times at high temperatures, unmolten polyamide 12 material ages during the manufacturing process. Hence, it needs to be refreshed with new material for further build cycles. In application, refresh rates of about 50 % are commonly used. In this work, the recycling optimized material PA 2221 from EOS is analyzed along a series of 13 build and refresh cycles using a reduced refresh rate of 32 %. Before and after every build, the powder is analyzed regarding melt properties determined by MVR and DSC measurements. Thereby, in-process ageing effects are investigated and the steady-state conditions are determined accordingly. In addition, powder properties are directly linked to resulting mechanical and geometrical part properties. Key findings are a robust DSC measurement method for polyamide 12 powder, constant “circulated” material properties after three build/refresh cycles and robust tensile properties along the whole tested powder life cycle. As a result, process conditions of PA 2221 using reduced refresh rates can be derived from this work.

## Introduction

In the polymer laser sintering process, unmolten polyamide 12 powder ages due to long process times at high temperatures. To ensure a constant powder quality, mixtures of new and aged (recycled) powders are commonly used. Since the ageing intensity of the recycled powder may vary from job to job due to different temperature histories, powder mixtures have to be qualified using measurement methods like the melt volume rate (MVR). For standard polyamide 12 powders like PA 2200, this results in a so-called refresh rate of about 50 %. Considering common part packing densities of only up to 10 %, a significant amount of powder cannot be used in further build jobs. This work addresses two topics: The aged powder specification by differential scanning calorimetry (DSC) and the characterization of a recycling optimized material (PA 2221) along a rising number of build cycles. Knowledge about the long term process behavior and methods to qualify powder mixtures are essential for a robust and reproducible process.

The following chapter about the state of the art focuses on previous work on ageing effects of polyamide 12, its influence on process quality and measurability. Then, the methods used in this work are described, for example the build job layout, process parameters and measurement methods. Thereby, the focus is on the development of a DSC measurement procedure to obtain accurate and reproducible values. The next chapter focuses on the results of powder and part analyses along the build cycles as well as the influence of different refresh rates. Finally, the results are summarized and an outlook is given in the last chapter.

## **State of the Art**

During the laser sintering process, unmolten polyamide 12 powder is exposed to high temperatures for very long times of up to many hours and days. This leads to chemical and physical ageing effects influencing material and particle properties. Important processes are a simultaneous thermal-oxidative induced reduction of the molecular chain length and a cross-linking due to post condensation. In previous studies, different methods have been tested to specify the ageing state of a powder. The most applied method is the measurement of the melt volume rate (MVR). The overall increase of the average molecular chain length of aged powder leads to an increase of the melt viscosity. This effect can also be observed measuring the solution viscosity of the polymer dissolved in sulfuric acid or m-kresol. In addition, the distribution of the molecular weight and its shift to higher weights due to ageing effects has been determined by gel permeation chromatography measurements. Regarding changes of particle properties, a reduction of powder flowability is observed. [1-9]

The impact of powder age on part properties has been the focus of different studies. Since the material ages differently depending on the build job layout and process parameters, individual refresh strategies are necessary to ensure constant powder qualities in application. Thereby, the adjustment of a defined melt volume rate (MVR) is a proven and recommended method. High melt viscosities of the mixed powder especially lead to surface defects on built parts, while the mechanical properties are quite robust. However, a determination of fixed “MVR limits” is difficult due to individual part quality requirements and testing machine adjustments. Also a cross influence between powder quality and process parameters has been observed. [2, 9-12]

Long term in-process ageing effects after many build cycles are another important aspect: Without refreshing, material ageing leads to significantly reduced mechanical properties, part densities and surface qualities. Equally, the MVR values decrease continuously. In contrast, refreshing of used material leads to constant powder qualities after a defined number of build cycles: For standard PA 2200 material and a refresh rate of 50 %, MVR values have been shown to level off to a constant value after three cycles. In general, the results show that a constant material quality can only be achieved via refresh strategies. [3, 11, 13]

In contrast to (melt) viscosity measurements, thermoanalytical methods applied on to differently aged laser sintering materials can be found in only a few studies. In this work, the most important method is the differential scanning calorimetry (DSC) analyzing temperature- and time-dependent melt and crystallization effects. For example, thermal ageing of polyamide 12 powder leads to an increase of the melt temperature and to a widening of the melt peak due to post-crystallization and a reduced mobility of the molecular chains. An additional reduction of the recrystallization temperature enlarges the process window. However, only little data about the impact on built parts along the powder life-cycle is available. [5, 13-14]

Summarizing the state of the art, much knowledge about chemical and physical ageing mechanisms using polyamide 12 material and their influence on part quality is available. However, material behavior after many build cycles using optimized materials with low refresh rates is quite unknown. Considering a higher average residual time of a powder within the process, the impact on process quality needs to be investigated in greater depth. Measurement methods like DSC may provide additional knowledge about the interaction between powder quality, process parameters and part quality. Thereby, the process performance and reproducibility can be improved.

### Experimental set-up

The main experimental approach in this study is a series of build and refresh cycles using PA 2221 material. The overall mixture ratio in each cycle is 32 % new powder, 9 % overflow powder and 59 % partcake powder. Before and after every cycle, the powder is analyzed regarding its melt flow rate and melt/recrystallization properties measured by Differential Scanning Calorimetry (DSC). The samples produced in every cycle allow for an additional analysis of part quality characteristics. Here, the mechanical tensile properties and the warpage intensity are given as indicators for the powder quality. A summary of the set process parameters and an overview about the build job layout are given in table 1. The refresh series is started with a part-less pre-ageing of material and ended after the 13<sup>th</sup> build cycle.

To study the influence of different refresh rates on melt properties, additional powder samples were mixed out of new powder, one time cycled (AP 0) and ten times cycled (AP 10) powder using different refresh rates from 0...100 %.

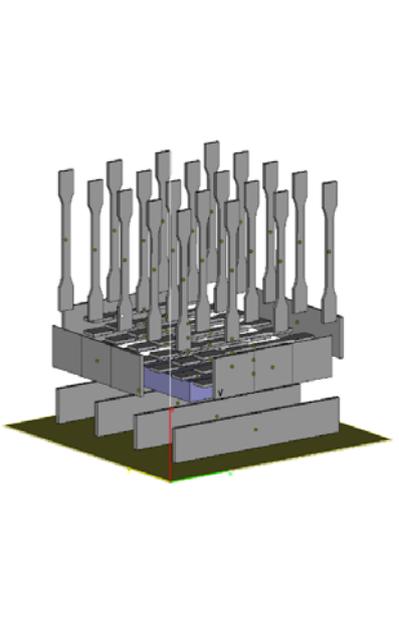
<b>build height</b>	300 mm	
<b>powder</b>	PA 2221, refreshed with 32% of new powder after every cycle	
<b>exposure parameters</b>	EOS Part Property Profile (PPP) “balance”	
<b>layer thickness</b>	120 µm	
<b>build temperature</b>	178 °C	
<b>Removal chamber temp.</b>	130 °C	
<b>build time</b>	~ 17 h 30 min	
<b>cooling phase</b>	10 h within machine (nitrogen) + >24 h outside (standard atmosphere) until <40°C	
<b>Post process</b>	Automated glass sphere blasting within a rotating cage	

Table 1: Process parameters and build job layout for the refresh series with PA 2221

The most common method to specify the powder age is the melt volume rate (MVR). Considering the occurrence of different ageing intensities within one job, all powder samples are taken out of well homogenized recycled and mixed powder. The powder is pre-dried for 30 min at 105 °C in standard atmosphere and tested at 235 °C with a load of 5 kg in a Zwick Mflow melt flow tester. This method is based on the DIN EN ISO 1133 test standard and EOS working instructions.

For the specification using the Differential Scanning Calorimetry (DSC), a measurement method is developed at first. Since it is known that the results of the DSC method may vary from sample to sample, a robust measurement method is essential when slight changes in the material have to be detected. Therefore, measurements of one homogenized recycled powder batch have been performed with different heating/cooling rates (10...20 K/min), sample mass (5...20 mg), pre-treatment methods (dried, conditioned, moisturized) and purge gas (nitrogen, air). The best

working combination, showing the lowest standard deviation between repeatedly tested specimens, is shown in table 2. In addition, fixed limits are defined for the analysis of integrals. Each powder sample is prepared and measured three times.

Measurement values of the DSC method include the melting/recrystallization enthalpy, the shape of the respective peaks and the peak temperatures. Here, the focus is on the peak height (distance between base line and max. peak), peak width (at 50% of peak height) and peak temperature during the first melt phase. These properties are most reproducible and show dependencies on the powder age along build cycles. For the recrystallization and second melt phase, powder properties show higher standard deviations and undefined trends.

<b>DSC equipment</b>	Mettler Toledo DSC 1, STAR <sup>e</sup> Excellence Software
<b>balance</b>	Mettler Toledo XS205 Dual Range
<b>crucible</b>	Aluminum, with pierced lid, volume 40 µl
<b>purge gas</b>	Nitrogen, 20 ml/min
<b>procedure</b>	1st heating – cooling – 2nd heating
<b>start/end temperature</b>	0...250 °C
<b>heating/cooling rate</b>	10 K/min
<b>conditioning</b>	no pre-treatment – stored in atmospheric humidity
<b>analysis limits</b>	1st heating: onset -50 K ... endset + 7 K cooling: endset -35 K ... onset + 7 K 2nd heating: onset -70 K ... endset + 5 K

Table 2: DSC measurement parameters

Mechanical part properties are determined according to DIN EN ISO 527 on an Instron 5569EH universal testing machine, equipped with parallel clamps and a video extensometer. The specimens have a cross sectional area of 4 x 10 mm<sup>2</sup>. The truss speed is set to 1 mm/min for the measurement of the Young's modulus (strain 0,05...0,25 %) and then accelerated to 50 mm/min for the measurement of the tensile strength and elongation at break. Directly after unpacking from the part cake, the specimens are vacuumed in plastic foil to prevent undefined conditioning effects, meaning that all tensile bars are tested dry. Tensile specimens are investigated in both upright (z) and flat (x) orientation. Each given value is the average of a minimum of 18 specimens.

The bottom area of the build jobs contains four rectangular specimens with a size of 250 x 42 x 6 mm<sup>3</sup>. In this area, warpage effects are typically most intense due to a higher in-process cooling rate compared to the upper areas of the part cake. Warpage of the test specimens is determined by measuring the up and down facing profile along the longest dimension. A second-degree polynomial function is approximated to these profiles, the pre-factor of which represents the warpage intensity.

## Results & Discussion

The following diagrams show the results of the powder and part analyses. For the refresh series, the focus is on the individual curve shapes to find out, if the properties approach a kind of “steady-state” condition after several build cycles or change continuously. In contrast, the investigation of different refresh rates provides information about general dependencies between powder quality and measured material parameters as well as the measurability itself.

The results of the MVR analyses are shown in figure 1. On the left side, the MVR value as function of build cycles is given. The top curve represents the melt volume rate of the homogenized refresh powder starting in cycle 1. The MVR value decreases until the 3<sup>rd</sup> cycle and levels off at  $\sim 21.5 \text{ cm}^3/10 \text{ min}$  afterwards. It can be concluded that the powder is in a more or less steady-state condition from the 4<sup>th</sup> cycle on. The homogenized aged powder shows lower MVR values, which level off already after the first build cycle at  $\sim 12 \text{ cm}^3/10 \text{ min}$ . The value at cycle 0 is thereby the result of the part-less pre-ageing of the powder. Regarding different refresh rates presented in the right diagram, the melt volume rate increases with rising refresh rates. The curve shows a nearly linear behavior between aged ( $16.2 \text{ cm}^3/10 \text{ min}$ ) and new powder ( $60.8 \text{ cm}^3/10 \text{ min}$ ).

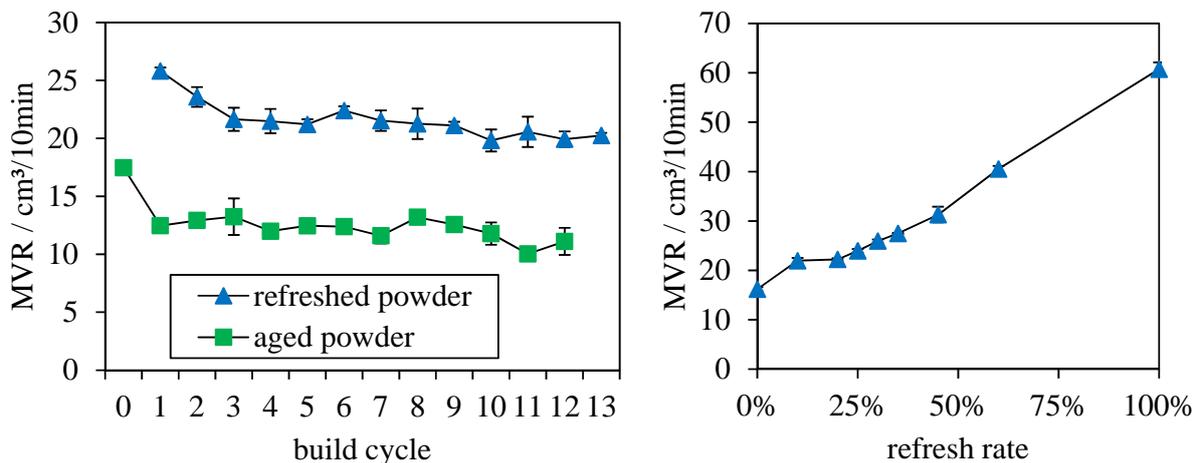


Figure 1: Melt Volume Rate (MVR) as function of build cycles and refresh rate

In the following diagrams (figure 2), the results of the DSC analysis is shown for the first heating of the aged powder as function of build cycles. Similar to the MVR values, the peak height, peak width and peak temperature change only until the 3<sup>rd</sup> build/refresh cycle and then level off to a steady-state condition. The values for new powder marked in red (cycle -1) correspond to the trends. The reduction of the peak height and increase of the peak width may be traced back to an enlarged variation of powder properties within the powder sample. This variation can be reasoned by the rising number of powder components with various cycle times on the one hand, but also by the occurrence of different ageing intensities within one job depending on the position within the part cake. Another effect may be differences in post-crystallization. In contrast, new powder shows a very sharp melt peak due to its only single component. Next to the peak shape, also a shift of the peak to higher temperatures is observed. Although these changes are only very small, they are measured repeatedly with a standard deviation of about 0.11 K. The peak temperature levels off to  $\sim 188 \text{ }^\circ\text{C}$ . The normalized integral representing the melt enthalpy shows no significant trend; the value for differently aged powder is on the same level like new powder.

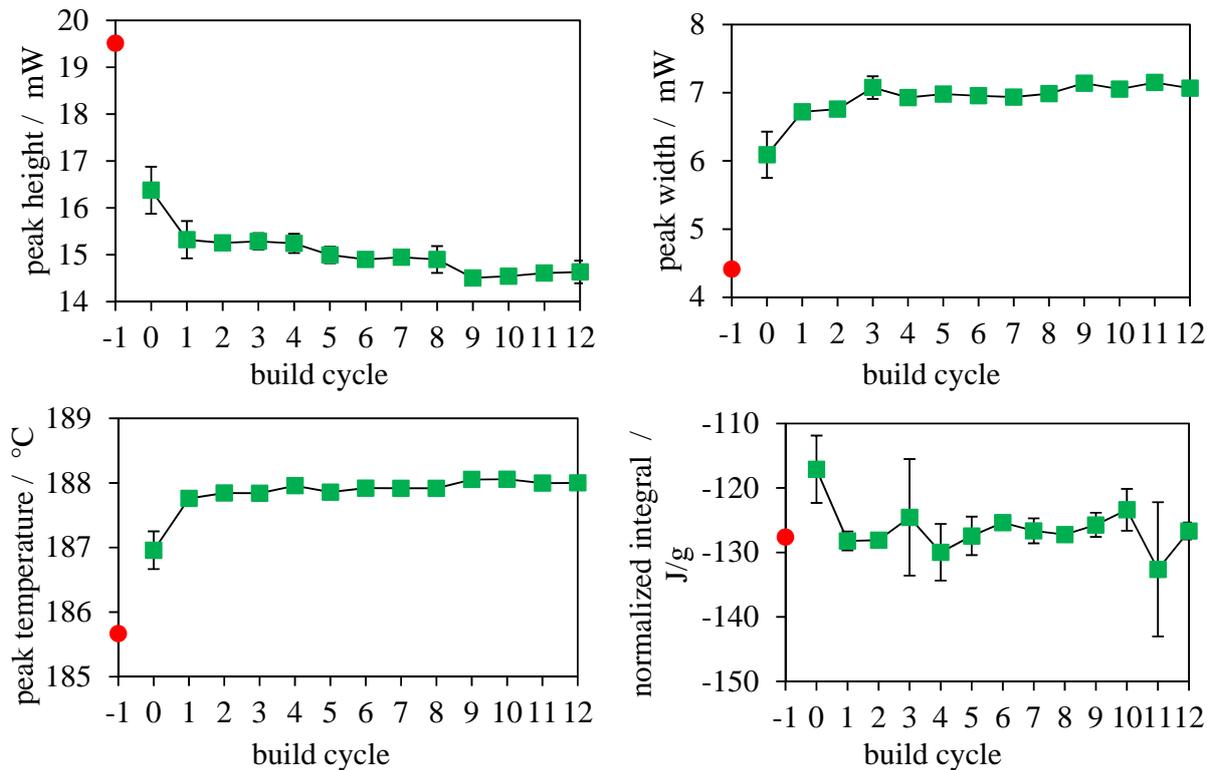


Figure 2: DSC analysis of recycled powder as function of build cycles – 1<sup>st</sup> heating

Next to the number of build cycles, different powder mixtures of new powder, one time cycled (AP 0) and ten times cycled (AP 10) powder were tested by DSC. Again, the results of the first heating phase are presented (figure 3). The peak height is nearly constant for aged and 25 % refreshed powder and increases for higher refresh rates. Thereby, the peak height is higher for mixtures made of new and less intensely aged powder (AP 0). The trend of the peak width also fits to these trends: The lower the refresh rate and the older the aged powder used for the mixtures, the wider and lower the peak shape. Regarding the peak temperature, the absolute difference between the tested powder samples is again very small. Nevertheless, low standard deviations allow an interpretation of a trend to lower peak temperatures with higher refresh rates. Here, no significant changes for the differently aged origin powders are detected. The melt integral shows no significant dependency of the melt enthalpy on the aged powder state or the refresh rate.

To conclude the DSC measurements of the aged powders from the build series and the different powder mixtures, some general trends are obvious. Especially the peak shape reacts sensitively to changes of the material: The more components with different ageing states are contained within the powder, the less sharp the melt peak. Also the melt peak temperature has been found to be sensitive to powder age, but less significantly so considering the relative change. The melt enthalpy has not been found to be suitable to detect powder ageing intensities as the standard deviations are high and the trend indefinite.

Comparing MVR and DSC measurements, the shapes of the curves match very well. After three build cycles, powder properties level off to a steady-state value and do not change even after 13 build and refresh cycles. Both increase in melt viscosity and widening/flattening of melt peaks may be traced back to an increase of the molecular weight induced by cross-linking and/or post-condensation of the polymer.

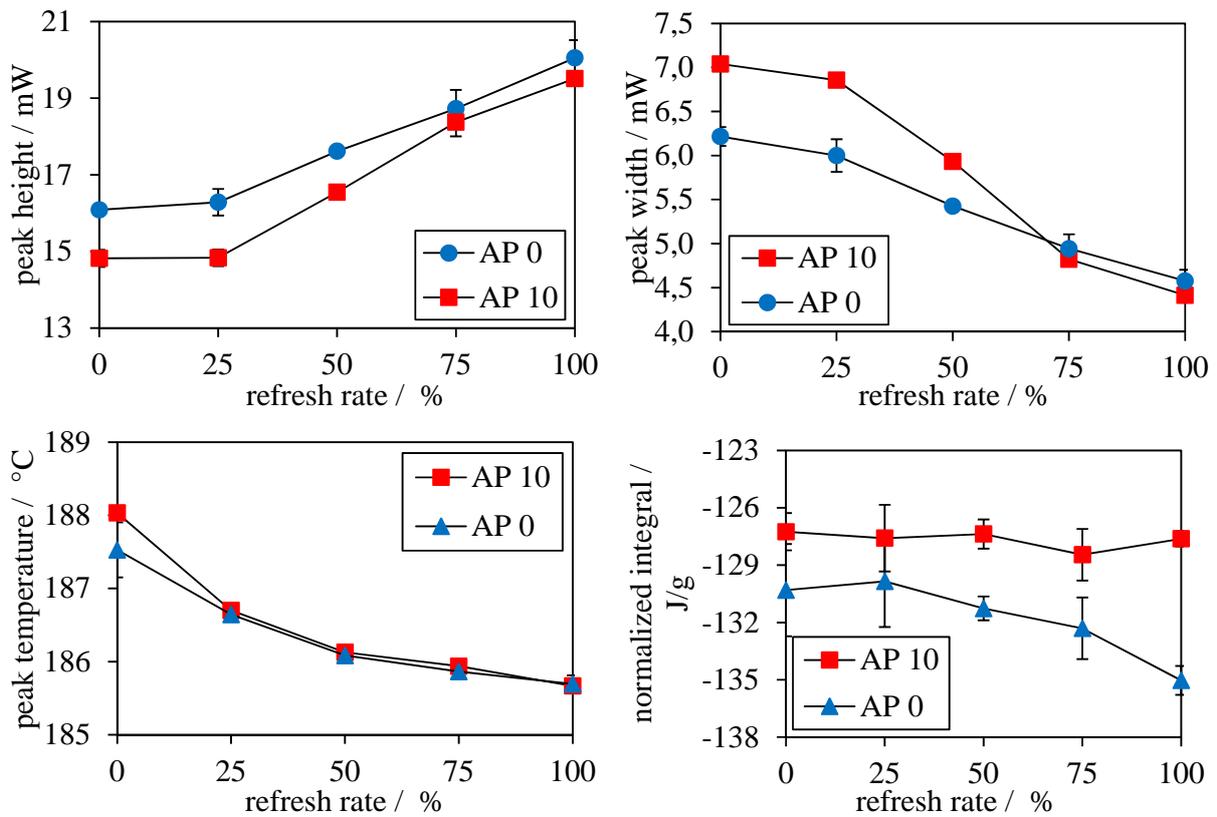


Figure 3: DSC analysis of different powder mixtures adjusted by refresh rate – 1<sup>st</sup> heating

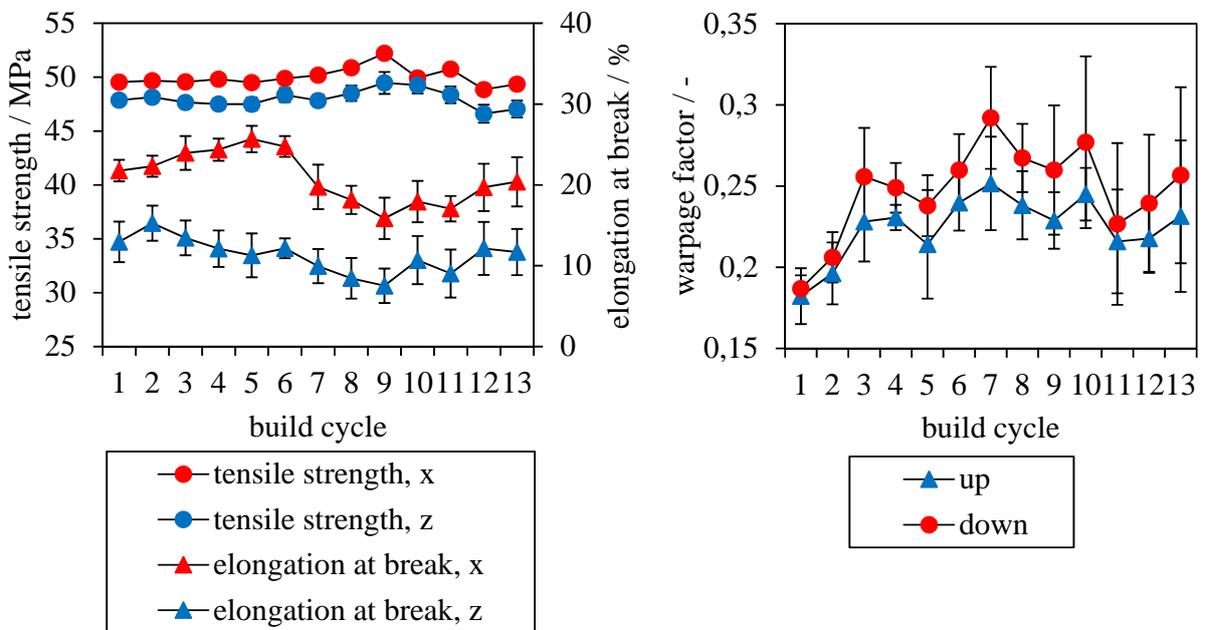


Figure 4: Mechanical tensile properties and warpage intensity as function of build cycles

Finally, part quality characteristics are examined along the build/refresh series. The static mechanical tensile properties are shown in figure 4, left. In both upright (z) and flat (x) direction, the tensile strength does not change with a rising number of build cycles. Regarding the elongation at break, the variation of the absolute values as well as the standard deviations are higher. Thereby, the properties in flat direction are generally higher compared to the upright direction. A slight but significant trend to more brittle properties is detected between the 7th and 9th build cycle. As already shown in past investigations, the elongation at break is much more sensitive to changes of the material or process conditions. However, the mechanical part properties cannot be linked to the powder qualities detected by MVR and DSC measurements.

Regarding geometrical part properties, the warpage intensity is analyzed (figure 4, right): During the first three build cycles, a trend to higher warpage intensities is detected. After that, the values level off showing much higher standard deviations. A correlation of powder quality and warpage intensity is possible.

### **Conclusions & Outlook**

In this work, a series of build and refresh cycles has been performed using PA 2221 material with a refresh rate of 32 %. Before and after every cycle, the mixed and used powder has been analyzed as well as part quality characteristics. The powder properties detected by MVR and DSC measurements level off after only three build/refresh cycles. Due to powder ageing effects, the MVR value and the melt peak height decrease, while an increase is observed in the melt peak width and temperature. The mechanical part properties are robust regarding the measured powder properties and do not change significantly along the build/refresh series. However, a link between powder conditions and warpage intensity is possible. Since no significant trend is detected after three build cycles in both powder and part properties, it can be concluded that the use of PA 2221 material is possible with reduced refresh rates, maintaining constant part quality characteristics.

In the future, more investigations on powder ageing effects and their influence on built parts are necessary. The work performed only considers one specific build job layout. Other layouts and process parameters will result in different temperature histories during the process and thereby induce other powder ageing effects. To understand these effects, an examination of the ageing kinetics of standard and optimized material needs to be performed. Also powder qualification methods have to be developed studying the influence of different refresh rates on part quality. Another focus is on achievable material properties for application in part design and optimization.

### **Acknowledgement**

The authors want to thank all industry partners of the DMRC as well as the federal state of North Rhine-Westphalia and the University of Paderborn for the financial and operational support within the project “AMP<sup>2</sup>: Advanced Additive Material and Part Properties – Reduced Refresh Rates & Cooling Process Regarding LS”. Special thanks for the continuous assistance and contribution of EOS GmbH, Evonik Industries and Phoenix Contact, especially Eduard Hermann.

## References

- [1] Dotchev, K; Yusoff, W.: Recycling of polyamide 12 based powders in the laser sintering process, In: Rapid Prototyping Journal, Vol. 15 Iss: 3, pp. 192-203, (2009).
- [2] Pham, D.T.; Dotchev, K.D.; Yusoff, W.A.Y.: Deterioration of polyamide powder properties in the laser sintering process, In: Proceedings of the Institution of Mechanical Engineers, Part C: Journal of Mechanical Engineering Science, 222/11 (2007).
- [3] Wudy, K.; Drummer, D.; Kühnlein, F.; Drexler, M.: Influence of degradation behavior of polyamide 12 powders in laser sintering process on produced parts, In: AIP Conf. Proc. 1593, pp. 691-695 (2014).
- [4] Drummer, D.; Wudy, K.; Drexler, M.: Modelling of the aging behavior of polyamide 12 powder during laser melting process, In: AIP Conf. Proc. 1664, 160007, (2015).
- [5] Drummer, D.; Kühnlein, F.; Rietzel, D.; Hüdler, G.: Untersuchung der Materialalterung bei pulverbasierten Schichtbauverfahren, In: RTejournal - Forum für Rapid Technologie, 7 (2010).
- [6] Rietzel, D.: Werkstoffverhalten und Prozessanalyse beim Laser-Sintern von Thermoplasten. Ph.D. Dissertation, Universität Erlangen-Nürnberg, Germany (2011).
- [7] Schmid, M.; Amado, A.; Wegener, K.: Materials perspective of polymers for additive manufacturing with selective laser sintering, In: Journal of Materials Research, Vol. 29, No. 17, Sep 14, pp. 1824-1832 (2014).
- [8] Rüsenberg, S.; Josupeit, S.; Schmid, H.-J.: A Method to Characterize the Quality of a Polymer Laser Sintering Process, In: Advances in Mechanical Engineering, Volume 6, ID 185374, (2014).
- [9] Rüsenberg, S.: Prozessqualifizierung zur verlässlichen Herstellung von Produkten im Polymer Lasersinterverfahren, Ph.D. Dissertation, Universität Paderborn, Germany (2015).
- [10] Josupeit, S.; Rüsenberg, S; Rupp, N.; Gessler, M.; Schmid, H.-J.: Thermal Ageing of Polyamide 12 used for Polymer Laser Sintering - Influence on Part Quality Characteristics. In: Proceedings of the Annual Technical Conference of the American Society of Plastics Engineers (ANTEC), pp 2383-2388, (2014).
- [11] Wegner, A; Witt, G.: Betrachtung zur Pulvernutzungsdauer beim Laser-Sintern und Einfluss der Prozessführung auf die Entstehung von Ausschussbauteilen, In: RTejournal - Forum für Rapid Technologie, 9 (2012).
- [12] VDI guideline 3405, page 1: Additive manufacturing processes, rapid manufacturing Laser sintering of polymer parts - Quality control, Beuth Verlag GmbH, Berlin, (2013).
- [13] Gornet, T.J.; Davis, K.R.; Starr, T.L.; Mulloy, K.M.: Characterization of laser sintering materials to determine process stability, In: Bourell, D. (ed.), Proceedings of the Solid Freeform Fabrication Symposium (SFF), pp. 546-553, (2002).
- [14] Mielicki, C.: Prozessnahes Qualitätsmanagement beim Lasersintern von Polyamid 12. Ph.D. Dissertation, Universität Duisburg-Essen, Germany (2014).