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# Influence of Degradation Behavior of Polyamide 12 Powders in Laser Sintering Process on Produced Parts

K. Wudy<sup>1\*</sup>, D. Drummer<sup>1</sup>, F. Kühnlein<sup>1</sup> and M. Drexler<sup>1</sup>

<sup>1</sup>*Institute of Polymer Technology, Friedrich-Alexander-University Erlangen-Nuernberg, Germany – info@lkt.uni-erlangen.de*

## Abstract

Additive manufacturing technologies, such as selective laser melting of polymers enable manufacturing of complex parts without tools and forms. Due to high temperature during processing, a degradation of the used plastic powder occurs. The unmolded material in the building chamber, the so-called partcake, can be removed from the finished component after building and reused for another process. To realize reproducible part properties refreshing of partcake powder is necessary.

This paper presents results on the investigations of degradation behavior of polyamide 12 powder during selective laser melting process. The influence of different ambient conditions, e.g. ambient air, nitrogen and vacuum, is investigated in a model experiment. Oven aged polymer powders were analyzed with regard to their process relevant material properties. Considered material properties are phase transition temperatures, melting viscosity or molecular weight.

The results of the investigations show, that the influence of high process temperatures on used material can be reduced using other ambient conditions. Process relevant material properties are minor affected by storage under vacuum. In addition to that the influence of different ambient conditions as well as a material pretreatment on the degradation behavior of sls materials, e.g. exclusion of intermolecular located oxygen, is analyzed.

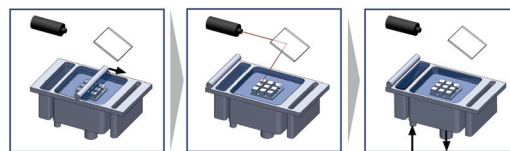
To correlate these results of the model experiment with real manufacturing process laser sintering experiments are done. PA12 powder is used for several building processes with refreshing. Produced specimens and resulting partcake powder are analyzed and correlated to the results of model experiment. Correlating effects, regarding process relevant material properties as well as aging influenced mechanical properties of specimens can be detected.

**Keywords:** degradation, polyamide 12, selective laser melting of polymers

## INTRODUCTION

Additive manufacturing techniques, such as selective laser melting of plastics, generate components directly from a CAD data set without using a specific mold. During the laser melting process components are built up layer by layer, which allows manufacturing of complex component geometries. Selective laser melting is widespread in rapid prototyping. Concerning individualization, the requirements posed to products have increased in recent years. More flexible manufacturing techniques step up the trend towards individualized serial products. Therefore a tendency towards rapid manufacturing of components for engineering applications has revealed. [1, 2]

The selective laser melting process can be divided into three sub-processes, powder coating, energy input and material consolidation. At first powder is applied in layers into a building chamber and heated up to a specific process temperature just below melting temperature of the polymer. Afterwards the cross-section of the component will be melted by using a CO<sub>2</sub> laser, while surrounding powder particles remain loosely in the building chamber. During laser melting process both melt and solid powder material is existent parallel over entire building time. After exposure the building chamber lowers by the thickness of one layer, e. g. 100 µm, and another powder layer is applied. Thus the structure will be build up layer by layer until the component is completed. [3]



**FIGURE 1:** Schematic process cycle of selective laser melting of polymers

Due to high building temperatures near the melting point of the used material physical and chemical degradation of the polymer can occur. Whereby physical degradation, a reversible process, changes the order of molecules and leads to post crystallization, relaxation and agglomeration. However, changes in the chemical structure of polymers like chain scission, branching or cross linking are caused by oxidation, post condensation and hydrolyses, so called chemical degradation phenomena. Known from injection molding chain scissions, branching and cross linking are major effects by polyamides. [4, 5]

Investigations on polyamide 6 and 66 reveal that at high temperatures and absence of oxygen cross linking caused by thermal degradation occurs predominantly [4]. As a consequence of that the molecular weight of the polymer increases.

The presence of oxygen leads to thermal-oxidative degradation effects. Due to high temperatures or shear stress polymer radicals will be generated under separation of hydrogen, which initializes the so called auto-oxidation-cycle. The created polymer radical

reacts with oxygen resulting in the formation of a peroxy radical. Afterwards a new polymer radical can be built with removing hydrogen from the backbone and creating a hydroperoxide. The activation energy for this reaction is high and the hydroperoxides formed have an endurance of a few seconds, whereby this determines the speed of the reaction. The weak O-O bond results in the formation of alkoxy radicals. In addition to that different transformation reactions of arisen radicals can occur. The alkoxy radicals can attack a hydrogen atom of the backbone and propagate the chain reaction on the one side or decompose with the formation of carbonyl compound on the other side. These reactions are responsible for chain scission, and the decrease of the molecular weight respectively. Chain reaction can be stopped in case of recombination of two alkyl radicals' and molecular weight will increase because of cross linking. The predominance of cross linking or chain scission depends on the used polymer itself. Investigations on oven aged polyamide 66 films revealed that the viscosity initially increases due to cross linking, followed by a decrease due to chain scissions [6]. [5, 7]

Because of the high specific surface of polymer powders shown investigations cannot be transferred to selective laser melting.

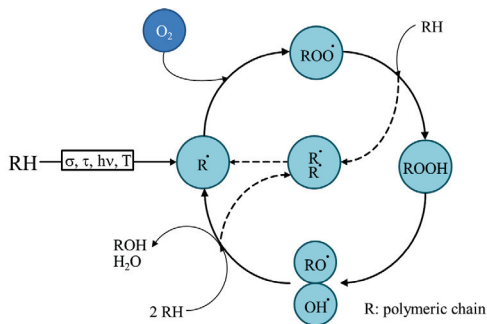


FIGURE 2: Auto-oxidation-cycle [7]

For a reproducible component manufacturing constant process conditions as well as constant base material properties are required. Aging effects during building process result in changes of the powder and polymer properties. Those affect process relevant material properties, e. g. viscosity and melting point as well as component properties, like surface roughness and mechanical behavior. Consequently varying component properties and limited process reproducibility are the consequences. Due to high costs of new powder material it is of special interest to reuse aged polymer powders. To enhance reproducibility of material properties, thus enabling a constant building process it is common to add new powder to the so called partcake material. Nowadays refreshing rates of 50 % new powder and partcake material are used to increase the process reproducibility. At first it is essential to understand the aging behavior of used PA 12 powder and subsequently generate tailored material properties, by using specific refreshing strategies. [8-11]

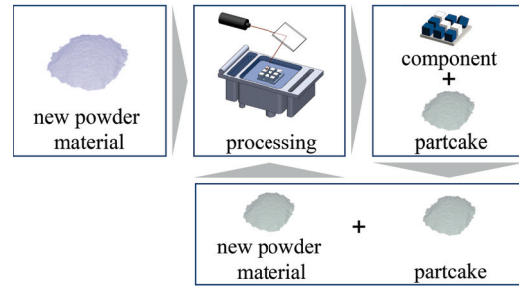


FIGURE 3: Refreshing strategy

#### Motivation

The construction of ready-to-use components by selective laser melting of plastics requires reproducible processes as well as constant material properties. Due to thermal and thermo-oxidative degradation of PA 12 powder a wide range of process relevant material parameters occur. The aging state depends mainly on the building chamber's temperature and the duration of building. The following investigations show the time dependent aging behavior of PA 12 laser melting powder. Therefore powders are stored in an oven under different environmental conditions (e. g. with regular air, vacuum and nitrogen) at building chamber temperature. Afterwards process relevant properties are analyzed. Processing experiments are conducted to analyze aging behavior of PA 12 powder during sinter process. To realize a less degradation of powder in laser melting process a specific refreshing strategy has been applied. Process relevant material properties as well as component properties were determined. To analyze aging behavior, which occurs during laser melting process, the results from processing experiments were compared with results from model experiments.

#### Material

In selective laser melting Polyamide 12 (PA 12) powder is used commercially, because of its powder flow behavior, low melt viscosity as well as wide range between melting and crystallization temperature. An unmodified PA 12 laser melting powder type PA 2200 from the supplier EOS GmbH, Germany, was chosen for model and processing experiments.

## EXPERIMENTAL

#### Model Experiments

Material is stored in an oven, to simulate the thermal stress during laser melting process under defined boundary conditions. To enable storage under ambient air, vacuum and nitrogen a heating cabin (type: VO200, company: Memmert, Germany) is used. Storage period was varied between 0, 8, 16, 32, 64 and 128 hours at a temperature of 175 °C just below the melting point of the used material.

To characterize PA 12 powder both before and after oven storage the process relevant material properties, e. g. melt flow behavior are determined. Melt flowability is essential in the phase of material

consolidation to generate dense components with high mechanical properties. Degradation and cross linking may cause change in average molecular weight, which can be determined with solution viscosity measurements (viscosity number) or melt volume rate (MVR). The viscosity number of PA 12 is determined with m-Cresol as solvent usually. In the following investigations sulfuric acid at 25 °C is used as solvent for solution viscosity measurements, due to security and health issues. The melt volume rate was measured according DIN EN ISO 1133 with a load of 21.6 kg at a temperature of 210 °C.

#### Processing Experiments

To enable subsequent characterization of the generated component, so-called Campus tensile bars are produced by selective laser melting (supplier: DTM, equipment: Sinterstation 200 type) following the DIN EN ISO 3167 (Type A) standard. Layer thickness is 100 µm, laser power 5 W, scanning speed 1257 mm/sec and powder application speed is 80 mm/sec. The same temperature of 175 °C as in the model experiments was applied in the build chamber. The height and resulting time of each building process was constant approximately 16 hours. After the first building process the aged powder material from the building chamber was reused for the second building process with a refreshing rate of 50 % new powder. This procedure was continued until the tenth building process. Thus, a very small percentage (0.2%) of the basic material of the tenth building job is already gone through nine processing steps. The mixture of 50 % new and 50 % aged powder was blended for 30 minutes in a rotary mixer at a revolution speed of 400 min<sup>-1</sup> to reach a homogeneous basic material. Flow behavior in the molten state is determined by analogy with the analysis of powder material in the model experiment. Therefore the viscosity number and melt volume rate was measured after the building process as well as refreshing.

#### Component Characterization

The test specimens' mechanical properties are determined in tensile tests at 5 mm/min test speed, in accordance with DIN EN ISO 527-1. The 5 test specimens are examined as to their modules of maximum stress and resulting tensile stress at break.

## RESULTS AND DISCUSSION

#### Model Experiments

To characterize flow behavior of the melt both before and after oven storage melt volume rate and viscosity number was determined. Figure 4 shows melt volume rate measurements of polyamide 12 powders in dependency of oven storage time. Unaged powder material is used as reference material. Overall all materials, stored up to 32 hours, show a decreasing melt volume rate, which can be traced back to occurring cross linking due to high storage temperatures of 175 °C. A low melt volume rate

represents a low flowability of the melt. Due to cross linking effect the average molecular mass of the polymer increases, which influences the melt flow behavior. With storage between 32 and 128 hours under air the melt volume rate increases. An increasing melt volume rate indicates shorter molecules and higher chain mobility due to chain scission. Under vacuum and nitrogen ambience the melt volume rate is not changing, which point out an equilibrium of cross linking and chain scission.

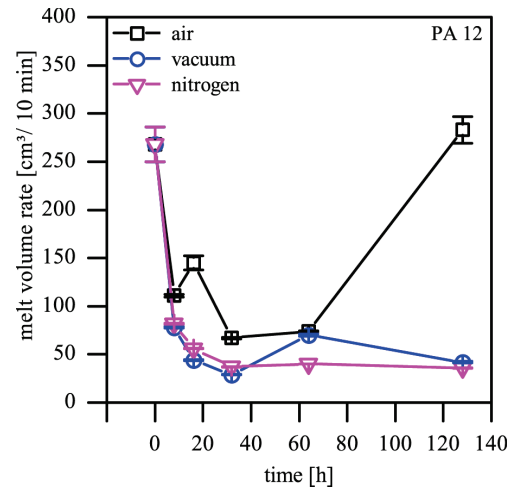


FIGURE 4: Melt volume rate in dependency of oven storage time

These material behavior can also be detected with measurements of the viscosity number, Figure 5. High viscosity numbers indicates a high molecular mass and a low flow behavior. Compared to melt volume rate viscosity number measurements are independent from water content. That is why usually the standard deviation is on a lower level. The viscosity number of all aged powders is higher than the viscosity number of the reference material. Up to 32 hours storage time the viscosity number of under air aged powder is on the rise and drops down afterwards.

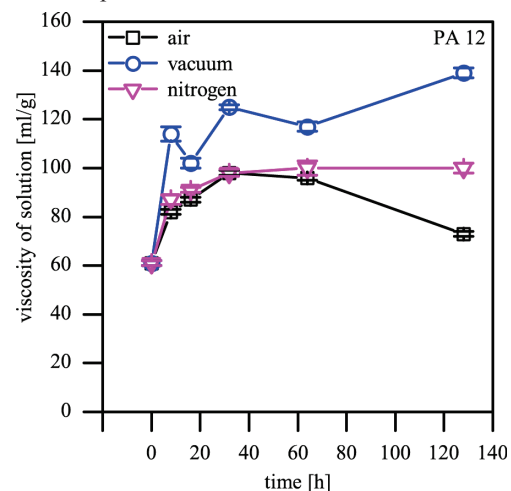


FIGURE 5: Viscosity number in dependency of oven storage time

Cross linking and chain scission occur simultaneously over the whole storage time, which process dominates depends on the ambient condition and storage time. At short storage times cross linking effects dominate whereas at long times chain scission is favored.

#### Processing Experiments

In a first step the aging behavior was characterized with oven storage experiments and in a second step the results were transferred to processing experiments. To compare the model with the processing experiments the building height and resulting time of each building process was constant approximately 16 hours.

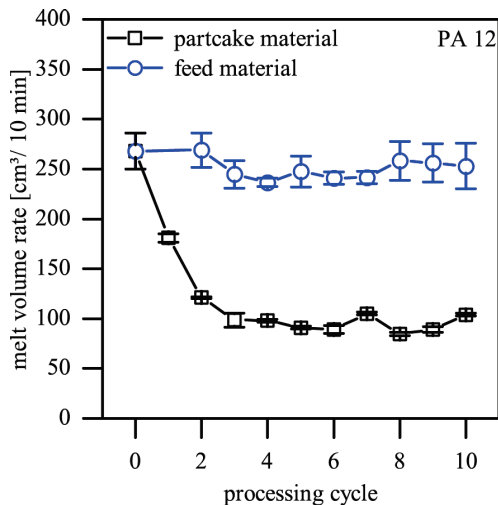


FIGURE 6: Melt volume rate in dependency of processing cycle

Figure 6 shows the melt volume rate in dependence on processing cycle for partcake and feed material. Feed material stands for the refreshed powder before a building process whereby the partcake material is the aged powder after the process. Due to high building chamber temperatures and resulting cross linking the melt volume rate of the aged powder is lower than the melt volume rate of reference material. The refreshed feed material has a melt volume rate just below the reference powder. As a result the addition of new powder material improves the flowability of the melt but it is not possible to achieve the melt volume rate of the reference material. A comparison of the model and processing experiments shows that during the processing cycle the cross linking effect dominates, because the melt volume rate sinks without any further increase by long storage times. Within the building process oxygen is excluded, hence auto-oxidation cannot proceed. After four processing cycles, a proportion of 12.5 % of the powder was exposed 64 hours at a temperature of 175 ° C. The fourth processing cycle shows in comparison to the 64 hours oven aged samples slightly higher melt flow rates due to the powder refreshing. Processing and model experiments show similar trends, but due to refreshing during sintering process the experiments cannot be compared directly.

In addition to melt volume rate measurements viscosity number measurements were conducted. In figure 7 viscosity numbers of partcake and feed material is represented. The material behavior shown with melt volume rate characterization can also be detected by analysis of the viscosity number. The aged powder has a higher viscosity number than the refreshed material, due to cross linking of the macromolecules. The refreshed powder attains a value between the reference and partcake material.

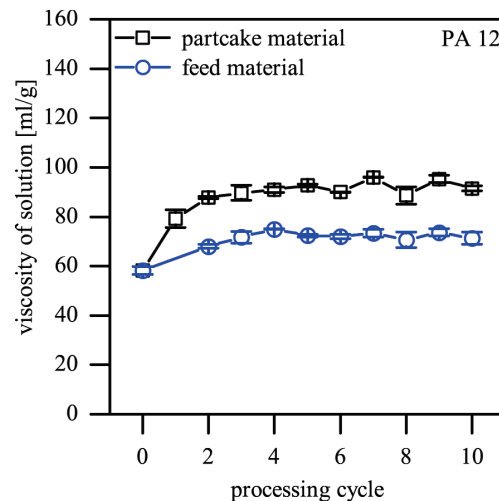


FIGURE 7: Viscosity number in dependency of processing cycle

#### Component Characterization

If a material system is to be applied for mechanically loaded components, its mechanical characteristics are the major criterion. The produced specimens show no plastic deformation, because the component fails prior to stretching. It is therefore impossible to obtain information on yield stress and elongation. In addition, the sintered specimens' real cross-sections cannot be determined, because specimens are porous. Indicated values of stress therefore refer to the cross-section of an ideally dense tensile test specimen.

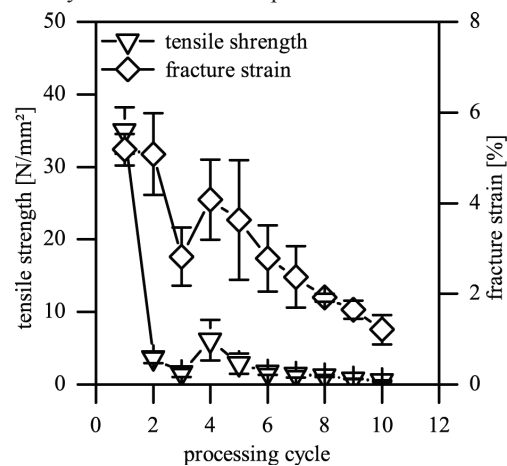


FIGURE 8: Mechanical properties of aged PA 12 tensile test specimen

In figure 8 the tensile strength and fracture strain of PA 12 tensile test specimen at different numbers of processing cycles are presented. The tensile strength declines after the first building processes. The determination of the specimen weight showed, that after the initial building process, the sample mass was halved. Thus the load bearing cross section was reduced and tensile strength declined. The dimensions of the specimen cross section were approximately the same thus porosity increases. The calculated tensile strength should therefore be corrected by a factor which depends on specimen porosity. Nevertheless tensile strength decreases with increasing number of processing cycles. This can be explained by the increase in average molecular weight and the associated reduction in the flowability of the melt. Due to this effect the connection between two layers is diminished. In addition to the tensile strength the fracture elongation declines from aging.

### CONCLUSION

The presented investigations show an influence of building chamber temperatures on material behavior of PA 12 powders. The model experiment reveals the correlations between process relevant material properties and ambient conditions. It can be said, that under oxygen, vacuum and nitrogen atmosphere in the first process hours cross linking is dominating. Whereas chain scission in particular occur at long storage times under oxygen. Cross linking of the material is a dominant effect during selections laser melting process. Powder refreshing will improve flowability of melt, but the aged powder is responsible for low mechanical properties.

These investigations form the basis of further research on the area of material degradation in selective laser melting of polymers. Influence of different ambient conditions and building temperatures as well as material treatment on the degradation behavior of PA 12 powder should be analyzed in the future. Fundamental understanding of the degradation process during selective laser melting are prerequisites for a systematically control of component properties.

### ACKNOWLEDGEMENT

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