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AGING BEHAVIOR OF POLYAMIDE 12: INTERRELATION BETWEEN BULK CHARACTERISTICS AND PART PROPERTIES

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Abstract

The high process temperatures in combination with long building times during the laser sintering process lead to chemical and physical aging mechanisms on the polymeric feed material. The unmolten partcake material, which acts as a supporting structure, can be removed after each building process and reused for further processes. However, material as well as bulk properties are changed due to thermal and mechanical load during the laser sintering process.

Within this paper the interrelation between the aging state, bulk values and resulting part properties like porosity, surface roughness and mechanical behavior are derived. Therefore, polyamide 12 powder is used for at least five processing cycles without refreshing. Before and after each building process, bulk characteristics and changes of the particle surface were determined. Specimens were manufactured during the laser sintering process in order to study the part density, roughness and mechanical behavior.

Introduction

Additive manufacturing technologies like selective laser sintering of thermoplastic powders generate components directly from a CAD dataset without needing a form or a mold. Therefore, the layer wise process of selective laser melting allows the generation of individualized complex parts with a serial character. Contrary to conventional manufacturing techniques like injection molding, which are optimized for high volume production and low unit costs, the costs for additive manufactured parts are almost independent from the degree of complexity and the quantity [1]. The advantages of additive technologies are favored for products with high customization, a high level of complexity and small lot sizes, which is known as “mass customization” [2].

Up to now, selective laser melting is widespread in prototype construction and is currently on the threshold of generating serial products in rapid manufacturing applications [1]. For the establishment of such techniques, in rapid manufacturing the main hurdles are a higher process reliability and reproducibility. Both characteristics are directly connected to the material behavior during laser melting process. Nowadays, merely one third of additive manufactured components are used in engineering applications as functional serial parts [3]. Nonetheless this application area shows the strongest rate of growth during the past years [3]. For this reason, in particular a fundamental understanding of the process itself and process material interaction is indispensable for increasing the amount of serial applications in the sector of additive manufacturing.

State of the art

In selective laser sintering incremental volume units in form of layers are build up in order the generate components without using a mold. Therefore, the thermoplastic polymer powder is selectively fused by a CO_2 laser. The process itself consists of the three sub-processes: powder coating, energy input and material consolidation. Firstly, a roller or knife system generates a powder layer in the build chamber, which is tempered to a specific process temperature just below the polymer's melting temperature. Secondly the cross-section of the component is melted by the use of a CO_2 laser, while the surrounding powder particles remain loosely in the build chamber, forming a supporting structure. After exposure, in the phase of material consolidation the build chamber lowers by the thickness of one layer, i.e. 100 µm in most cases and a new powder layer is applied. Step by step, these sub-processes are repeated until the component is completed. Following a cooling phase, the component is then withdrawn from the build chamber. [4, 5]

During the laser melting process the thermoplastic polymer powder has to endure a thermal stress, which is determined by the build chamber temperature and the building time. According to the model of quasi-isothermal laser melting process, the build chamber is preheated to a temperature between the melting and crystallization point of the semi crystalline thermoplastic. As a consequence, physical and chemical degradation of the polymer can take place. Physical degradation, a reversible process, changes the order of molecules and leads to post crystallization, concentration changes and agglomeration. Changes in the chemical structure of polymers like chain scission, branching or cross-linking are caused by oxidation, post-condensation and hydrolyses are so called chemical degradation phenomena. [6-8]

Investigations on oven aged polyamide 12 laser sinter powder reveal an increase of viscosity number due to thermally induced post condensation reaction under nitrogen and vacuum atmosphere for short periods of storage time near the beginning of melting [9, 10]. The storage under oxygen for short periods of time leads to an increase and afterwards to a decrease of the average molecular weight due to competing chain branching and scission mechanisms [9, 10]. The influence of storage time and temperature on oven stored polyamide 12 powder on the average molecular weight, the melt volume rate and thermal material properties like melting point was investigated in [11] from Pham. He shows that the crystallinity decreases and the melt volume rate increases with the storage time and temperature. In addition, Dotchev's [12] findings confirm the increase of viscosity with increasing time and temperature, probably due to post condensation reaction. Furthermore, Dotchev [12] investigated the correlation between building height, refreshing strategy, powder position and aging state of polyamide powder. Reaction kinetics of the solid state post-condensation of polyamide 12 powder and the prediction of the viscosity dependent on building time and temperature are investigated in [13]. In this paper the authors were able to derive a time and temperature dependent aging model for the process of selective laser melting.

Furthermore, previous investigations dealt with the influence of the amount of build processes or rather building time on rheological and bulk material properties as well as on part properties of polyamide 12 [14]. During the first building processes the elongation at break rises significantly, reaches a maximum and drops down sharply afterwards [14]. Gornet [15] also dealt with the influence of the amount of processing cycles on thermal, rheological and mechanical material properties. Wegner et al. [16] compared oven storage experiments with aging during laser melting process in order to establish a simple method to simulate the aging process. Therefore, aging processes at two different sintering systems were performed in order to analyze the correlation between material quality, process parameters and part properties. Josupeit [17] determined the influence of different powder aging states, adjusted with varying refreshing rates on mechanical properties of laser molten parts. Furthermore, Starr et al. [18] analyzed the influence of virgin powder and refreshed or blended powder on mechanical characteristics. No significant difference between virgin and blended powder can be detected in any mechanical property [18]. Zarringhalam et al. [19] studied the microstructure of laser sintered parts made of virgin, aged and refreshed powder with microscopic and thermal methods.

Methodology

Material

For the following investigations an unmodified virgin polyamide 12 (PA12) powder type PA 2200 from the supplier EOS GmbH, Germany is used. In order to obtain significant and reproducible results, new powder material with an equal lot number is used.

Processing conditions

The build processes were carried out at a research sintering system, which was build up by means of the Collaborative Research Center 814 – Additive Manufacturing, which is homed at the Friedrich-Alexander University Erlangen-Nürnberg. The research sintering system is equipped with a CO_2 laser with a wavelength of 10.6 µm, a maximum laser power of 50 watts and a focus diameter of 400 µm from the supplier Synrad. In order to achieve a homogeneous powder surface temperature distribution, the system is provided with a multiple heating system with eight infrared heating zones.

Beside the build chamber temperature (172 °C), the energy density (0.35 J/mm^3), the laser power (7.8 W), the scan speed (904 mm/s), the layer thickness (100 µm), the powder application speed (250 mm/sec), the hatch distance (250 µm) as well as the building height (75 mm) were held constant during the building process. A constant number of six tensile test specimens were produced within each manufacturing process to avoid changes of the thermal load.

The correlation between thermal stress time or rather number of processing cycle and aging behavior or the partcake powder, as well as on resulting part properties like mechanical behavior, density and surface roughness were determined. Therefore, virgin PA12 powder was processed five times without refreshing. Approximately only 60 per cent by weight of the feed material of a building process becomes partcake material. The other 40 per cent is used for component generation or is transferred to the over flow container. By means of this at the beginning ten equal manufacturing processes were built with virgin PA12 powder at the beginning. The sieved and mixed (30 minutes, 400 revolutions per minute) powder from these processes form the basis for further processing cycles. The accumulated thermal stress time the powder has to endure can be calculated from the period of each building process. Additionally, the temperature of the powder bed surface is observed by a pyrometer during the whole manufacturing process. The detailed design of experiments is shown in table 1.

Table 1. Design of Experiments

process cycle	build temperature (°C)	build time (h)	cumulative build time (h)
1	172	8.4	8.4
2	172	8.4	16.8
3	172	8.4	25.2
4	172	8.4	33.6
5	172	8.4	42.0

Characterization of material properties

After each build process material properties, e. g. bulk density, Hausner ratio and viscosity number were analyzed in order to determine the process relevant aging mechanism. According to DIN EN ISO 60 [20] the bulk density after and before each build process is measured. The bulk density is defined as the mass of the polymer particles divided by the total volume they occupy. For the analysis a bulk density tester from Emmeran Karg Industrietechnik type ADP is used. The average was calculated out of at least five measurements.

The Hausner ratio, a dimensionless parameter to characterize the compressibility of bulk materials, is defined as the quotient of tap and bulk density. The tap density was analyzed according to DIN EN ISO 787-11. Contrary to the norm the densification was realized via manual tapping. For this work a standardized number of at least 100 taps over a period of 5 min was used. The experiments were carried out under ambient conditions. Five runs build the basis for calculation of average Hausner ratio and root mean square deviation. According to Abdullah [21] the Hauser ratio indicates the flowability of powder materials. The best flowability is obtained when a bulk material does not condense. In this case the tap density equals the bulk density and the Hausner ratio is one. With increasing Hausner ratio the flowability of the bulk material declines.

In the laser melting process the bonding of two layers and thus the mechanical properties are fundamentally dependent on the viscosity of the polymer melt. A high melt viscosity leads to insufficient bonding, which results in low mechanical properties. To characterize the changes in the viscosity and thus the average molecular weight due to solid state post-condensation, the viscosity number of the virgin and aged powder is determined. The viscosity number of PA 12 is usually determined with m-Cresol as a solvent. Due to security and health issues sulfuric acid at 25 °C is used in the following investigations.

Characterization of part properties

In order to set up a correlation between powder properties and resulting mechanical characteristics intermediate values like porosity and surface roughness have to be determined. The component density was analyzed by determining the specimen dimensions and weight. The dimensions of the specimen for density measurements are 10 x 10 x 4 mm. Out of five specimens the average density was calculated.

The surface roughness of the tensile test bars was measured with a laser scanning microscope type LEXT OLS4100 form Olympus Corporation. A measurement field of 650 x 650 µm is resulting with a lens with 20x magnification. The area related average surface roughness S_z utilized at three different positions at the final manufactured layer of the test specimen.

According to DIN EN ISO 527-1, the test specimens’ mechanical properties are determined in tensile tests at a test speed of 5 mm/min. The test speed for the determination of the Young's modulus is 1 mm/min. The 5 test specimens are examined to their elastic moduli, maximum stresses and elongations at break. The samples are dried at 70 °C in a vacuum oven in order to create constant boundary conditions. The moisture content of the samples after the oven storage is measured with Karl Fischer titration and reached a value of 0.2 wt.-%.

The morphology and inner structure of the manufactured components were illustrated on 10 µm cross sections via transmitted light microscopy.

Results and discussion

Bulk properties like, bulk density and Hauser ratio of the basic material affect the mechanical behavior of laser molten parts. In addition, bulk properties are dependent on the aging state of the used polymer powder. Hence, bulk density and Hausner ratio are determined for powder that has endured varied thermal stress time in selective laser sintering process. Figure 1 represents the bulk density and the Hausner ratio for increasing cumulative build time. The bulk density decreases with rising thermal stress time, whereby the Hausner ratio shows a vice versa trend. A consequence of the lower bulk density will be a reduced specimen density. The rise of the Hausner ratio goes along with reduced powder flowability and thus a poor surface quality of the coated layer. Both mechanisms might influence the mechanical properties of the laser sintered parts.

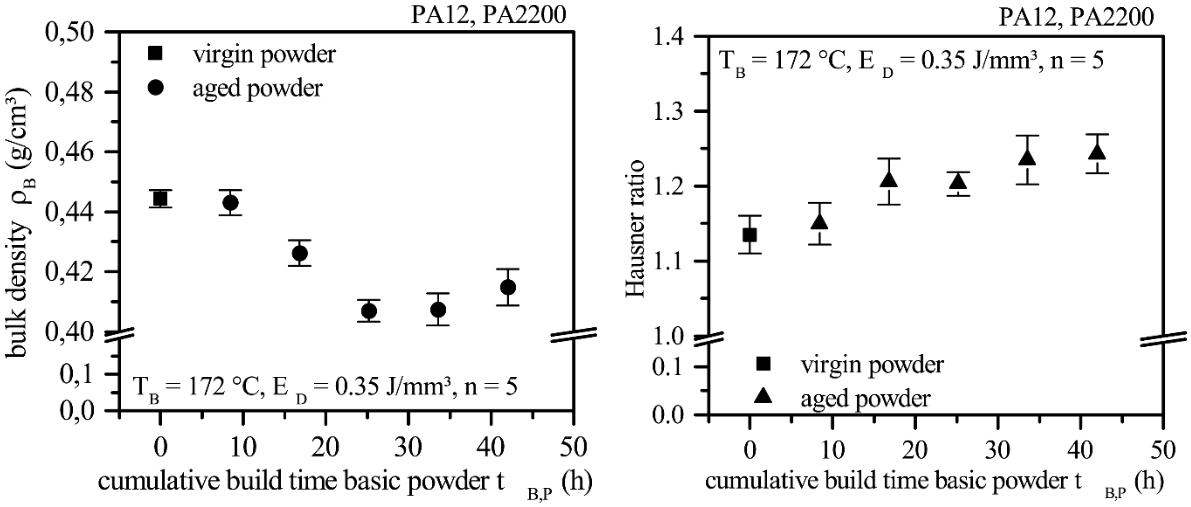


Figure 1. Bulk density and Hausner ratio of aged PA12 powder dependent on cumulative build time

The reason for the reduced bulk density are manifold. There might be a change in the particle size or in the particles surface for example. Therefore, Figure 2 shows the volumetric particle size distribution of the aged powders.

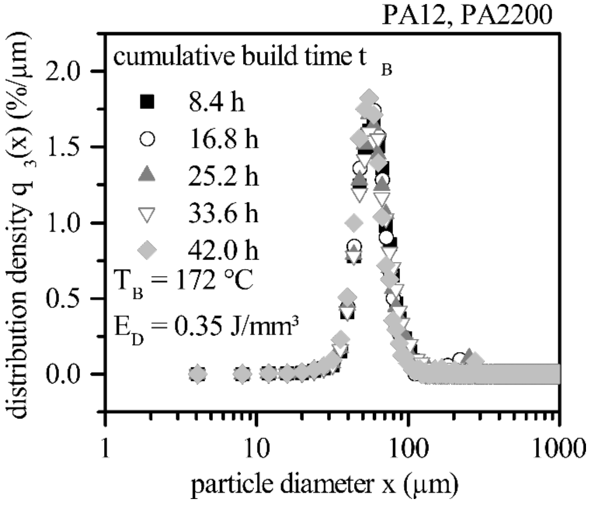


Figure 2. Particles size distribution of aged powder dependent on cumulative build time

With increasing cumulative build time, the particles size distribution is unchanged. Hence, the theory that changed particle size is responsible for the reduced bulk density can be excluded. Mielicki [22] confirms these results. For powder oven aged at a temperature of 174 °C neither the particle size nor the particle form changes with increasing storage time [22]. Nevertheless, for high storage times the deviation of form factors like the aspect ratio rises, which indicates variation in the particle form or surface [20]. Beside unchanged particle sizes the curves show a narrow particles size distribution, which is favored for high bulk and thus high component densities.

Beside shifted particles size distribution, changes of the particles surface could be responsible for the decrease of bulk density with increasing cumulative build time. Commercially available PA12 powder like Duraform PA from 3d Systems is adhered with fumed silica to enhance particle flowability and thus generate higher bulk densities [1]. The adhered fumed silica on the particle surface acts as spacer and reduces the adhesion force between the particles. Therefore, the flowability and the bulk density rises. Changes of the concentration of fumed silica may affect the powder flowability. That is why the particle surface is shown in Figure 3 via scanning electron microscopy images with a magnification of 1,000 and 10,000.

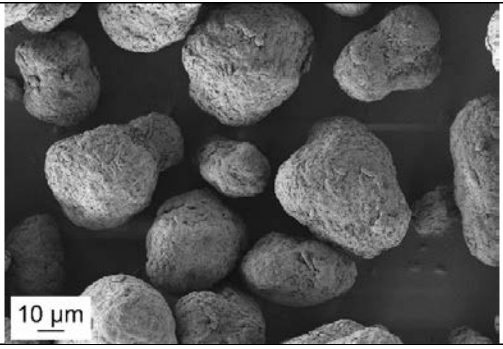
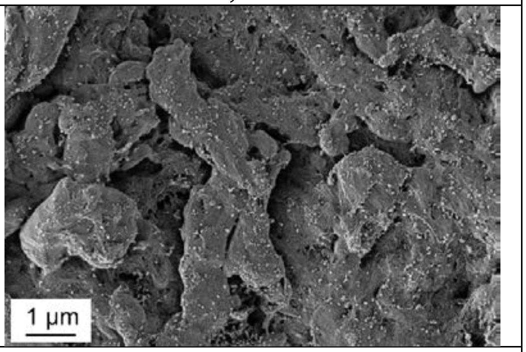
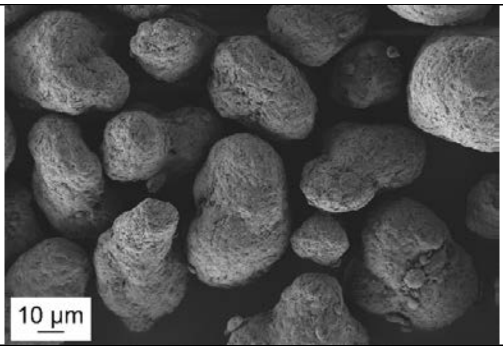
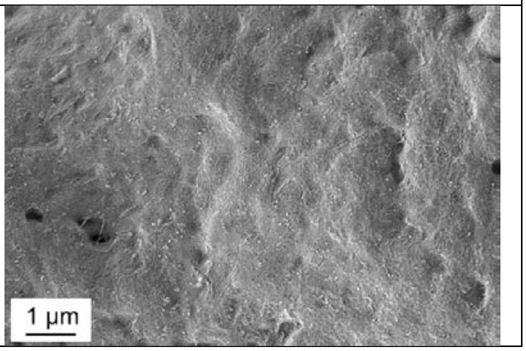
	magnification	
	1,000 x	10,000 x
virgin powder		
aged powder (cumulative build time 42.0 h)		

Figure 3. Scanning electron microscopy pictures of virgin and aged PA12 powder particles

With a magnification of 1,000 between the virgin and aged powder no differences can be obtained. A closer look at the particles surface reveals significant differences of the two powders. For high thermal stress times in a laser sintering system the particle surface is smooth and a fewer amount of adhered nano scaled particles, assumed as fumed silica, is visible. Both effects, the changes in particles surface and the reduction of fumed silica evoke that the distance between the particles is less and thus the adhesion force will be enlarged. Higher adhesion forces signify lower bulk densities and a reduced flowability. Hence, the increase of the bulk density can be traced back to a change of particle surface. However, the reduction of powder flowability will presumably affect the process stability and reproducibility in a negative way and the increasing bulk material porosity will lead to less dense parts.

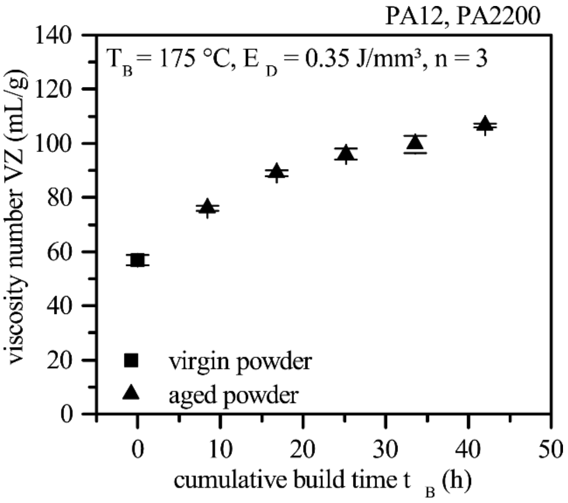


Figure 4. Viscosity number of aged PA12 powder dependent on cumulative build time

Beside reduced bulk density rheological characteristics like viscosity number changes with the thermal stress time, Figure 4. The materials' viscosity is fundamental for the bonding between two layers and hence for the mechanical properties of the laser molten parts. With increasing cumulative build time, the viscosity number rises until a steady state is reached. The rise of the viscosity number can be in all likelihood traced back to post condensation processes shown for example in [14]. The average molecular weight rises due to post condensation reaction, where stored monomers react with chain ends with a high molecular mobility. According to the Mark-Houwink-Equation also known as Kuhn-Mark-Houwink-Sakurada-Equation (Equation 1) with increasing molecular weight the intrinsic viscosity strives against a limit [23]. This correlation is valid for a structural coefficient αbetween 1 and 0.6, which is the case for polymer solutions [23].

$$[\eta] = K \cdot M^{\alpha} \quad \text{Equation 1}$$

With increasing viscosity, the sinter behavior as well as the bubble removal time in selective laser sintering is changed. According to the Frenkel's theory of sintering with increasing viscosity the time for particle coalescence rises [24]. Additionally, the bubble removal time in a polymer melt increases for rising viscosity, which is known from rotational molding [25]. Both effects affect the time until a homogeneous melted layer in laser sintering is formed and thus influences the component density.

Therefore, the component density is evaluated for different cumulative build times of the used basic powder in order to find a correlation between bulk and part properties dependent on the aging time, Figure 5. With increasing thermal stress time of the PA12 powder the density of the produced parts decreases. At the one hand the reduction of part density is related with the lower bulk density. On the other hand, due to higher viscosity and molecular weight the bubble removal time and the coalescence time rises, which indicates a higher bubble concentration at the end of a building process. Investigation on polyethylene particles via rotational molding reveals that for decreasing melt volume rates and increasing average molecular weight, the time for the disappearing of trapped air will be longer [26]. Both effects, the lower bulk density and the higher viscosity for longer thermal stress times of the PA12 basic powder signify a reduced part density, which is represented in Figure 5.

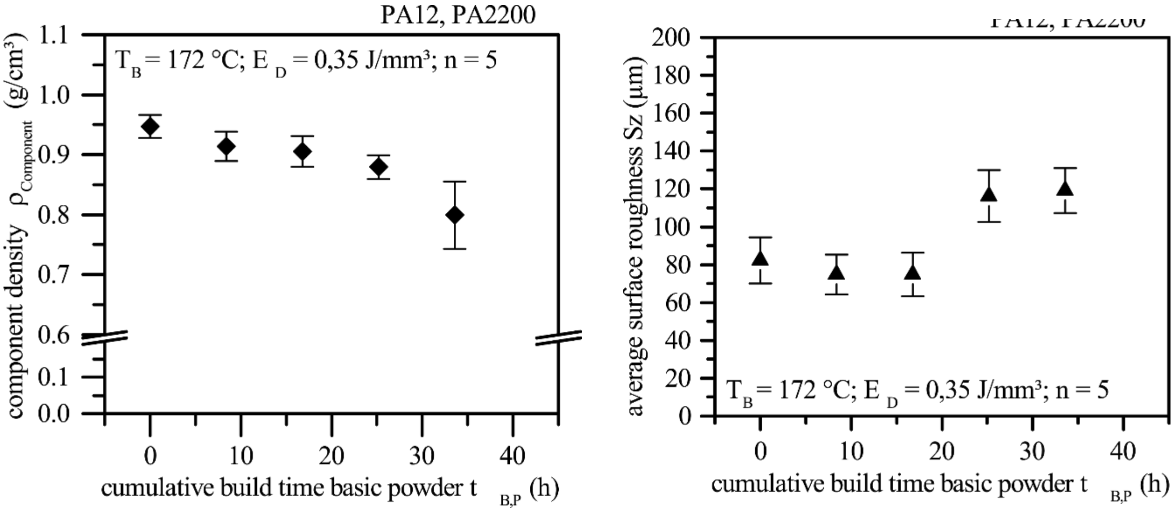


Figure 5. Component density and surface roughness of laser molten specimen built with aged PA12 powder with varying cumulative build time

In addition to component density the average surface roughness S_z of the via laser sintering produced specimen is influenced by the cumulative build time of the used basic powder, Figure 5. For high cumulative build times of the used powder the surfaces roughness rises from 80 µm to approximately 120 µm, which is an increase of 50 %. With increasing viscosity of the melt the resistance to embed particles on the top layer is heightened, which may cause different surface roughness.

Both the reduced component density and the raised surface roughness may influence mechanical properties. Pores as well as embedded particles act as defects and stress peaks, which triggers fracture. In the case of rapid manufacturing applications, resulting mechanical part properties of the laser molten parts are of main importance. Hence, Figure 6 represents the tensile tests of specimen produced with powder with different thermal stress time.

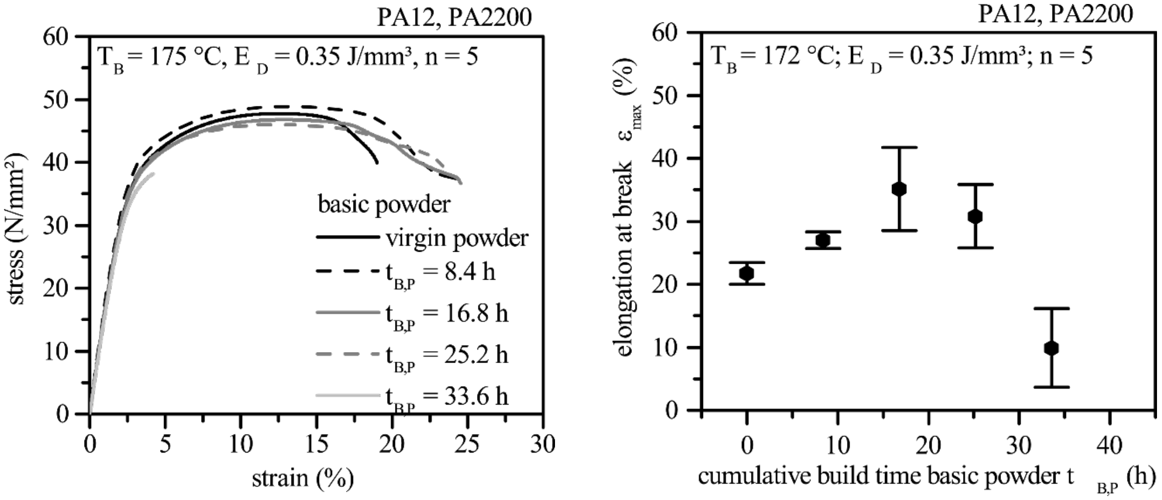


Figure 6. Representative tensile test curves and elongation at break of laser molten specimens build with aged PA12 powder with varying cumulative build time

Figure 6 shows representative stress strain curves of laser sintered specimens produced with PA12 powder, which has endured different thermal stress times. With increasing cumulative build time, the stress strain curves show a significant change in fracture behavior. An initially ductile material behavior changes with increasing powder aging to a brittle performance. This transformation in fracture behavior is also visible by analyzing the elongation at break dependent on cumulative build time of the used PA12 powder. The elongation at break increases up to a powder aging state of the feed material of 16 hours and drops down sharply afterwards. Figure 4 reveals that with increasing cumulative build time the viscosity number und thus the average molecular weight increases, probably due to post-condensation reaction. This increase of molecular weight due to storage at temperatures near the beginning of melting of the polymer leads to longer distances in which the chains can slide past each other and thus the elongation at break raises. For cumulative build times higher than 20 h the bulk density decreases sharply. This goes along with increasing part porosity and surface roughness. As a result of all these effects the elongation at break drop down. Finally, the increasing porosity and surface roughness are superimposing effects and mechanical part characteristics collapse. Furthermore, microstructural changes, that are not analyzed yet, may occur and have an influence on the mechanical behavior.

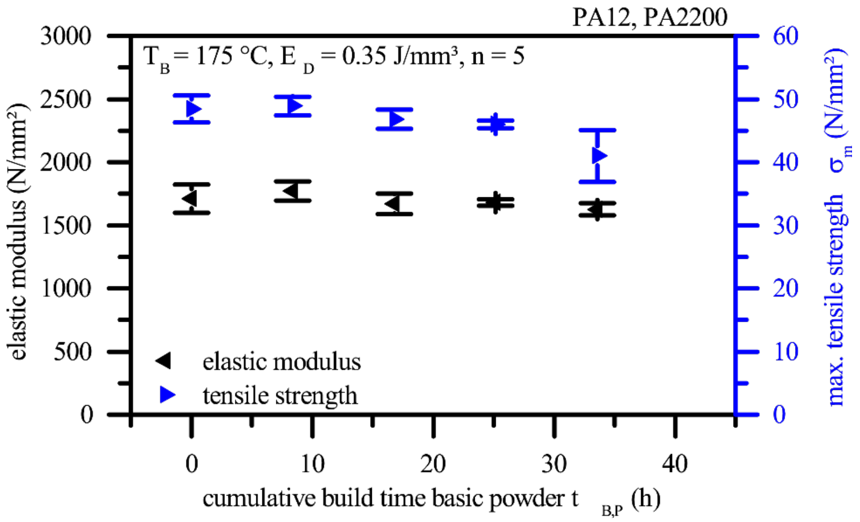


Figure 7. Elastic modulus and max. tensile strength of laser molten specimen build with aged PA12 powder with varying cumulative build time

Figure 7 exhibits the mechanical properties elastic modulus and maximum tensile strength as a function of the powder aging state of the feed material. Both characteristics, the elastic modulus and the tensile strength, are not influenced by the powder aging state of the used basic material. The abidance on a stable level is not surprising because both characteristic values do not act as a feasible indicator for the aging state of the material [6].

Figure 8 shows transmitted light microscopy images of laser sintered polyamide 12 specimen. The cumulative build time of the basic powder for specimen production rises from the left to right side. Specimen build with virgin powder represent pores and unmolten particles, which exhibit under polarized light in a yellowish appearance. Furthermore, the build direction is visible due to layer wise appearance. As a result of high number of unmolten particles within the component the elongation of break reaches a lower level than for the specimen, which has endured a higher thermal stress. Nevertheless, the unmolten particles have almost the same density as the raw material. That is why the density of the parts is almost constant during the first build processes. Notwithstanding, the unmolten particles act as defects and elongation at break is reduced.

With increasing cumulative build time of the basic powder the unmolten particles disappear and the single layers are no longer visible. A rising amount of molten material signifies an increase in the elongation at break. Further increase of the cumulative build time of the basic powder leads to a high amount of huge pores, a reduction of density and thus reduced mechanical characteristics.

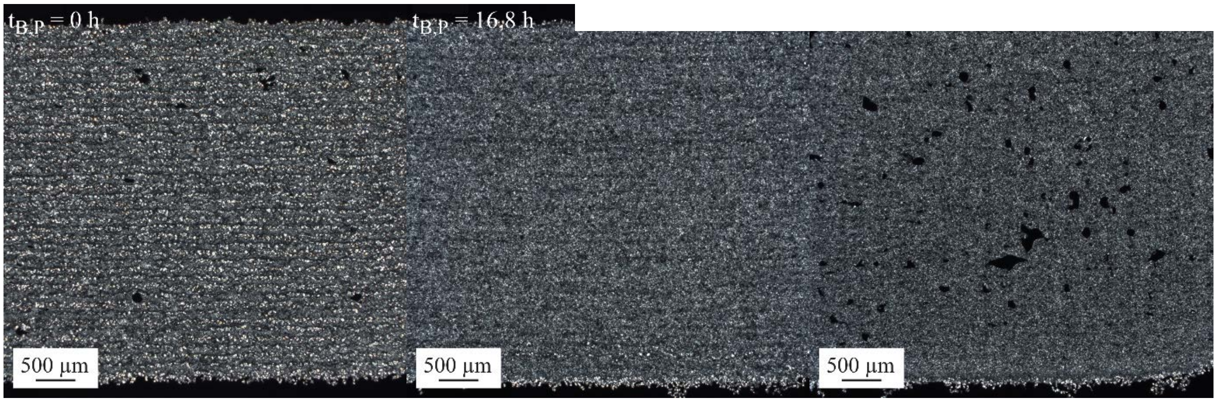


Figure 8. Transmitted light microscopy images of laser molten specimen build with aged PA12 powder with varying cumulative build time

Conclusions

Within this paper the influence of build time or rather cumulative build time on the aging state of polyamide 12 paper and its influence on mechanical properties are investigated. Therefore, material is reused until it has been going through five processing cycles without refreshing. Before and after each laser melting process, the bulk and material properties are analyzed. In addition, mechanical part characteristics are determined in order to correlate them with the powder aging state.

With increasing cumulative build time, the bulk density decreases and the Hauser ratio increases by constant particle size distribution. This change of bulk properties with increasing aging time can be traced back to changes of the particles surface due to partial melting or incorporation of the nano scaled additive on the particle surface. In addition, viscosity increases due to high temperature during laser melting process with increasing cumulative build time. Probably this effect is caused by post-condensation reaction of the polyamide.

Furthermore, a decline of the part density and an increase of the surface roughness can be detected with increasing cumulative build time. These superimposing effects lead to a change in the elongation of break. With increasing aging time of the used feed powder, the elongation at break passes a maximum and declines sharply afterwards. Due to the increase of the viscosity number and the reduction of the amount of unmolten particles the elongation at break rises initially. The reduction of the bearing cross section due to higher porosity, in combination with higher surface roughness, leads to the decrease of elongation at break. Elastic moduli as well as maximum tensile strength are not influenced by the aging state of the feed material.

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