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Influence of energy input on degradation behavior of plastic components manufactured by selective laser melting

Dietmar Drummer[a,b], Katrin Wudy[a,b,*], Maximilian Drexler[a,b]

[a]*Collaborative Research Center 814 – Additive Manufacturing, Am Weichselgarten 9, 91058 Erlangen, Germany*
[b]*Institute of Polymer Technology, Friedrich-Alexander-Universität Erlangen-Nürnberg, Am Weichselgarten 9, 91058 Erlangen, Germany*

Abstract

Additive manufacturing techniques, such as selective laser melting of plastics, generate components directly from a CAD data set without using a specific mold. High building chamber temperatures in combination with long building times lead to physical and chemical degradation of the surrounding powder and the manufactured component in the case of selective laser melting of polyamide 12 (PA12).
Thus the following investigations show the influence of energy densities on mechanical properties as well as on the aging behavior of the manufactured components. Therefore several building processes with varying energy densities will be conducted. Aged polymer components were analyzed with physical, thermo analytical and mechanical methods with regards to their process relevant material properties. Considered material properties for example are phase transition temperatures, melting viscosity or molecular weight. The basic understanding of the influence of energy input on material properties will lead to new process strategies with minimized polymer degradation.

Peer-review under responsibility of the Bayerisches Laserzentrum GmbH

Keywords: Selective laser melting; polyamide 12; aging; energy density

* Katrin Wudy. Tel.: +49-9131-8529736 ; fax: +49-9131-8529709 .
E-mail address: wudy@lkt.uni-erlangen.de

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1. Introduction

Additive manufacturing techniques such as selective laser melting of semi-crystalline thermoplastics allow generating components directly from a CAD data set without needing a specific mold. Components are built up layer by layer during the laser melting process, whereby manufacturing of complex component geometries is possible. In rapid prototyping selective laser melting is widespread. Additive manufacturing techniques are established in prototype construction, in particular. A tendency has recently revealed towards the rapid manufacturing of components for engineering applications. [1, 2]

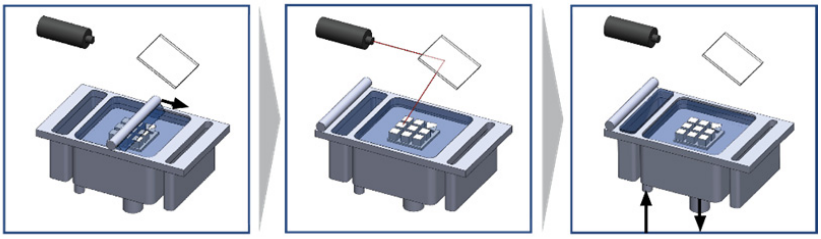

Fig. 1. Schematic process cycle of selective laser melting of polymers.

The characteristic feature of additive manufacturing is the building of incremental volume units in layers, aimed at generating components with complex geometries and undercuts. Therefore the process of selective laser melting can be divided into three sub-processes: powder coating, energy input and material consolidation (Figure 1). First powder is applied in layers into a building chamber by using a roll or knife system. Additionally the building chamber is heated up to a specific process temperature just below the melting temperature of the polymer. Secondly a specific cross-section of the component will be molten by using a CO_2 laser, while the surrounding powder particles remain loosely in the build chamber, forming a supporting structure. Afterwards the building chamber lowers by the thickness of one layer, e. g. 100 µm, and another powder layer is applied. Step by step, this process is repeated until the component is completed. Thus the component will be built up layer by layer. [3, 4]

2. State of the Art

The process of selective laser melting determines certain requirements the material has to fulfil. One of them is that both melt and solid material exist over the entire period of building. To achieve this two-phase mixture area, the build chamber is pre-heated to just below the crystalline melting point of the used material, according to the model of quasi-isothermal laser sintering [5]. As a consequence of this 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. [6-8]

In the case of polyamide 6 and 66 a storage at high temperatures near the melting point and absence of oxygen lead predominantly to cross linking caused by thermal degradation and thermal initialized post condensation effects [6]. As a result the molecular weight of the polymer will rise. However, the presence of oxygen leads to thermal-oxidative degradation, which can be described by the auto-oxidation cycle. Whether cross linking or chain scission is predominant during the auto-oxidation process depends on the used polymer mainly. 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 [9]. [8, 10]

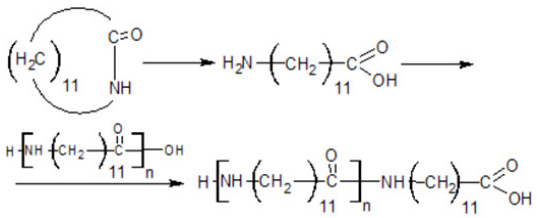

Fig. 2. Reaction scheme of the post condenzation of polyamide 12.

Due to the high specific surface of polymer powders shown investigations on polymer films or components cannot be transferred directly to selective laser melting process. Griskey [11] showed the increase of the average molecular weight in dependency of temperature and time under nitrogen atmosphere due to post condenzation also known as solid state polycondenzation for polyamide 66 chips. A scheme of the post condenzation of polyamide 12 is shown in figure 2. Gaymans [12] analyzed both the time and temperature dependence of the mechanism and kinetics of solid state polymerization on polyamide 6 particles (average size 0.2 – 0.5 mm) for a wide temperature range between 110 and 205 °C.

Previous investigations on oven aged polyamide 12 powder for selective laser melting showed that for short periods of storage near the crystalline melting point thermally induced post condensation dominates under vacuum and nitrogen atmosphere [13, 14]. Whereas storage periods over 64 hours lead to an increase of the molecular weight due to chain scission [13, 14]. Furthermore the influence of the amount of building cycles on thermal and rheological material properties were analyzed by the same authors [15]. The rheological behavior has the highest change in the first building processes and reaches a stable level afterwards [15]. As well Gornet [16] dealt with the influence of the amount of processing cycles on thermal, rheological and mechanical material properties. The correlation between building height, refreshing strategy, powder position and aging state of polyamide powder was investigated by Dotchev [17].

However, none of these authors is focused on the influence of the energy input on the aging behavior of the powder and component material. To close this gap, the authors of this paper would like to show the influence of several strategies of energy input on the aging state of the powder and component material. Additionally mechanical properties will be measured in dependency of the energy input, to link the aging state of the component material to mechanical properties.

3. Motivation

To produce ready-to-use components with selective laser melting reproducible powder and thus component properties are inalienable. However, aging effects during the building process are responsible for changes of powder and polymer properties. Due to thermal and thermo-oxidative degradation of PA 12 powder a wide range of process relevant material parameters occur. Degradation effects affect those process relevant material properties, e. g. melt viscosity as well as component properties, like surface roughness and mechanical behavior. Results of this are varying component properties and limited process reproducibility. The aging state of the powder is influenced by many factors, e. g. the exposure, the building chamber temperature and the duration of building. The understanding of the aging behavior of used Polyamide 12 powder is therefore essential. [18-20]

The following investigations show the interaction between the energy input going along with exposure, mechanical properties and polymer degradation within the component. Several building processes with varying energy densities during exposure will be conducted to analyze the influence of energy input on mechanical properties and the aging state of the manufactured components. The energy density is varied by changing laser power or scanning speed. On the one hand an increase of the laser power would for example result in a heightening of the temperature of the exposed cross section, whereby post condensation kinetics will be speeded up. Additionally high temperatures of the exposed cross section are responsible for thermal degradation effects like chain scission. Therefore the aim of the investigations is to find a correlation between mechanical properties and the aging state of manufactured parts.

4. Experimental Setup

4.1. Material

Reasons for using Polyamide 12 (PA 12) powder in selective laser melting might be its powder flow behavior, low melt viscosity as well as wide range between melting and crystallization temperature [21]. For the following investigations an within these investigations unmodified PA 12 laser melting powder type PA 2200 form the supplier EOS GmbH, Germany, was chosen. In order to obtain significant and reproducible results new powder material with equal lot number is used.

4.2. Processing

During building process, so-called Campus tensile bars are produced by selective laser melting with varying energy density. Layer thickness (100 µm), powder application speed (250 mm/sec), hatch distance (250 µm) as well as building chamber temperature (172 °C) were held constant. Temperature measurements of the building area using thermographic camera have shown that the surface powder bed temperature is between 170 and 174 °C. The height of each building process was constant. The resulting energy density ED is defined as following:

$$E_D = \frac{P_L}{v_s \cdot h_s \cdot d} \tag{1}$$

with laser power P_L, scan speed v_s, hatch distance h_s and layer thickness d. Investigations by Rietzel [21] showed that laser power and scan speed are the most influencing factors on mechanical properties in selective laser melting of PA 12. Because of this these two parameters were chosen to analyse the influence on aging behaviour of PA 12 components during laser melting process. Several building processes with varying scan speed and laser powder were conducted first and the then resulting mechanical properties and the aging state of the manufactured parts were measured. Table 1 shows the detailed design of experiments:

Table 1. Design of Experiments.

Test number	Laser power [W]	Scanning speed [mm/s]	Energy density [J/mm³]
1	4.5	904	0.20
2	7.8	904	0.35
3	11.3	904	0.50
4	13.6	904	0.60
5	7.8	1582	0.20
6	7.8	904	0.35
7	7.8	633	0.50
8	7.8	527	0.60

4.3. Component Characterization

In the phase of material consolidation melt flowability is essential to generate dense components with good mechanical properties. Degradation and cross linking may cause a change in average molecular weight, which can be determined with solution viscosity measurements (viscosity number). The viscosity number of PA 12 is usually determined with m-Cresol as solvent . In the following investigations sulfuric acid at 25 °C is used as solvent for the solution viscosity measurements, due to security and health issues.

To determine the mechanical behavior of the tensile test bars, tensile tests according to DIN EN ISO 527-1 are performed by using the tensile testing machine Zwick 1465 (Zwick GmbH & Co.) and a test speed of 5 mm/min. The 5 test specimens are examined as to their modules of elasticity, maximum stress and resulting tensile stress at break. Before testing, the test specimens were stored at 70 °C under vacuum atmosphere for more than one week to avoid an influence of the water content on the mechanical properties of polyamide 12 samples. The water content of the specimen was analyzed by Karl Fischer titration after drying. The water content of all component was just below

0,2 wt-%. Additionally the component density is analyzed by determining the weight and the dimensions of produced specimen (80 x 10 x 4 mm).

5. Results and Discussion

In order to evaluate the mechanical properties, the component density has to be determined and analyzed at first. Since the component porosity determines the load-bearing cross section within the tensile test and thus affects the resulting strengths and modulus. Therefore in figure 3 the component density in dependency of the energy density is represented. The energy density is on the one hand changed by laser power (figure 3, black) and on the other hand by scanning speed (figure 3, blue). With increasing energy density respectively laser power the component density lingers at a constant level within the measurement accuracy, figure 3. In contrast, a reduction of the scanning speed and thus an increase of the energy density lead to varying component densities, figure 3. High energy densities as well as low energy densities result in low component densities. In the case of a low scanning speed the exposure time is reduced, thus the polymer material is not melted completely and as a consequence the component porosity rises. For high energy densities the exposure time increases and thermal induced degradation effects like chain scission may occur. Consequently, high as well as low energy densities will lead to a reduction of component density and an optimum of the part density is in this case reached at an energy density of 0,35 J/mm³.

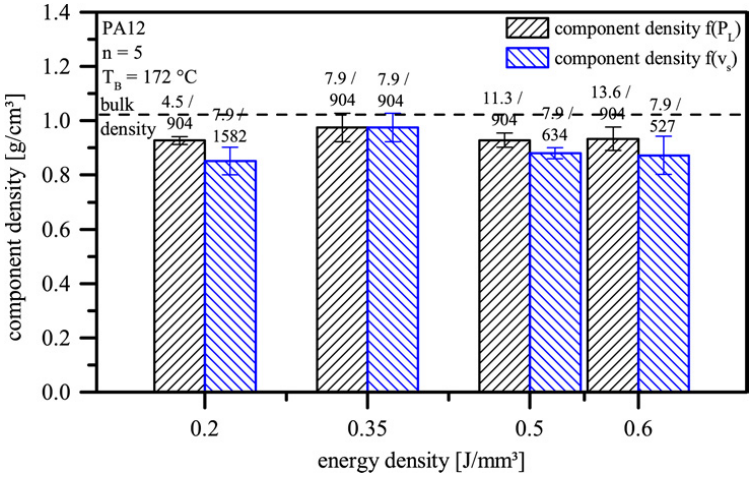

Fig. 3. Component density in dependency of energy density changed by laser power and scanning speed.

To establish a link between the aging state of the component during laser melting process and the resulting mechanical properties, viscosity of solution measurements are conducted. In this context figure 4 shows the relationship between the aging level of the component represented by the viscosity of solution and the introduced energy. An increase of the energy density respectively laser power leads to slightly lower viscosities of solution. A reduction of the viscosity of solution indicates a decrease of the molecular weight of the polymeric material. Higher cross section temperatures during exposure due to a higher energy input may for example lead to thermal induced degradation effects like chain scission and thus a lower average molecular weight. A similar effect can be seen by changing the scanning speed, figure 4. With increasing energy densities the viscosity of solution decreases and thus the molecular weight decreases. A reduction of the scanning speed leads to a higher exposure time and thus to higher cross section temperatures of the exposed layer. As a consequence the total building time and the component temperature during processing rises. Due to these two effects chain scission can take place and the average molecular weight of the produced components is affected. Changes in the average molecular weight may influence the mechanical part properties in a second step. Therefore mechanical material properties and the aging state represented as viscosity of solution were compared afterwards.

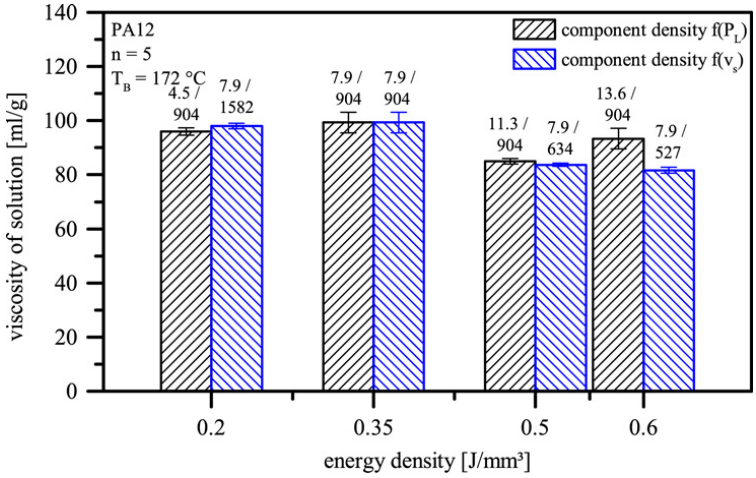

Fig. 4. Viscosity of solution in dependency of energy density changed by laser power and scanning speed.

If a material is to be applied for mechanically loaded components, its mechanical characteristics are the major criterion. Figure 3 shows the mechanical material properties maximum tensile strength, elongation at break and elastic modulus in dependency of energy density, which is changed by laser power. First of all it has to be mentioned that the sintered specimens' real cross-sections cannot be determined, because of its porosity. The indicated values of stress therefore refer to the cross-section of an ideally dense tensile test specimen. Taking root mean square deviation into account, maximum tensile strength as well as elastic modulus lingers at a constant level for varying energy densities, see figure 5. Even for low energy densities of 0.2 J/mm³ the maximum tensile strength and the elastic modulus reaches with 51 N/mm² and 1850 N/mm² a high level. This is not surprising because the tensile strength as well as the elastic modulus acts not as a feasible indicator for the aging state of the material [8]. However, elongation at break can be used as a value to characterize embrittlement and thus material degradation behavior. As a consequence of this a completely different behavior is reflected by evaluating the elongation of break. A low energy density leads to a low elongation at break with a high root mean square deviation. Responsible in this case are not the degradation effects of the polymer but the insufficient bonding of layers and the formation of defects in the part. Both for low and high energy densities the elongation of break decreases. The reduction of the elongation of break for high energy densities can be explained by the embrittlement of the material due to a lowering of the average molecular weight.

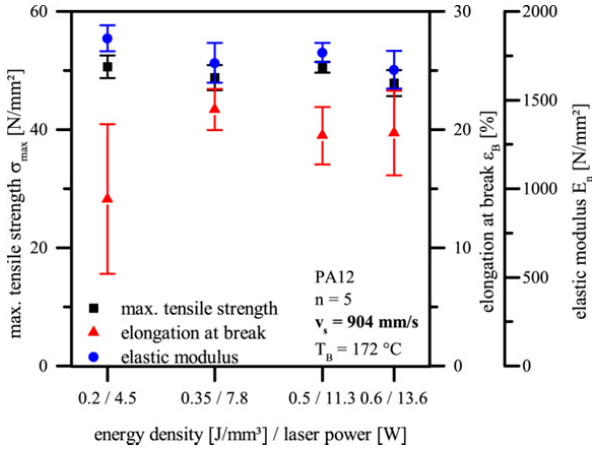

Fig. 5. Maximum tensile strength, elongation at break and elastic modulus in dependency of energy density changed by laser power.

In figure 6 the correlation between energy input respectively scanning speed and mechanical properties of laser molten parts is shown. For a low energy density and along going high scanning speed the maximum tensile strength, the elongation at break and the elastic modulus reaches a minimal point. These results go along with the measurements of the component density (figure 3). For this parameter setting the highest porosity is resulting, whereby the bearing cross-section in the tensile test is lower and thus maximum strength as well as elastic modulus decline. Whereas maximum tensile strength and elastic modulus for energy densities between 0.35 and 0.6 J/mm³ hardly changes. However, the elongation at break decreases for energy densities between 0.35 and 0.6 J/mm³. This effect can be explained by analyzes of the viscosity of solution. With increasing energy input the average molecular weight decreases due to degradation effects and an embrittlement of the material occurs. A result of the embrittlement is a reduction of the elongation of break. Thus the investigations exhibit that there is a correlation of mechanical part properties and the aging state of the components. Both analyzing methods, the tensile test and the viscosity of solution can be used to determine the aging state of the components in dependency of the aging state.

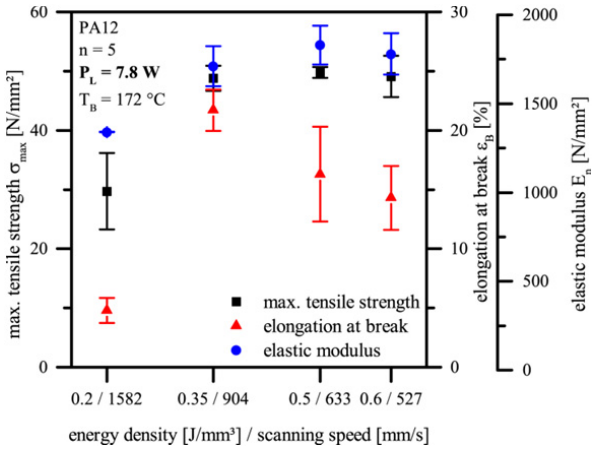

Fig. 6. Maximum tensile strength, elongation at break and elastic modulus in dependency of energy density changed by scanning speed.

6. Conclusion

The presented investigations show an influence of energy input altered by laser power and scanning speed on the aging state and mechanical properties of laser molten PA12 part. In a first step the component density of the produced parts was analyzed. The authors showed that the component density decreases for high as well as for low energy densities and reaches a maximum at 0.35 J/mm³. Furthermore the experiments reveal the correlations between the aging state represented as viscosity of solution and mechanical part properties. An increase in the energy density leads to changes in the average molecular weight and influences the mechanical properties expressed by a decrease of the elongation at break. Thermal induced chain scission maybe responsible for these changes of viscosity and breaking elongation. Maximum tensile strength and elastic modulus does not change due to degradation of the material during laser melting process. Within this investigation the authors linked mechanical part properties and aging state of the manufactured components together and could confirm the degradation of the polymeric material for high energy densities. These investigations form the basis of further research on the area of material degradation in selective laser melting of polymers. Influence of additional parameters e. g. different building chamber temperatures on mechanical material properties to avoid polymer degradation 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.

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References

[1] Gebhardt, A., 2004. Grundlagen des Rapid Prototyping. RTejournal 1, 1 - 16.

[2] Wohlers, T., Wohlers Report 2009 - Rapid Prototyping - State of the Industry, 2009.

[3] A. Gerbhardt, A., 2007. Generative Fertigungsverfahren : Rapid Prototyping - Rapid Tooling - Rapid Manufacturing. XVI, 499 S. Hanser: München, 2007. - ISBN 3446226664 (Gb.) 9783446226661

[4] Verl, A., Rommel, S.,Wolf, A., Becker, R., Beuninger, J., 2012. Generative Fertigung mit Kunststoffen: Konzeption und Konstruktion durch Selektives Lasersintern. Springer Verlag: Berlin, 2012.

[5] Alscher, G., 2000. Das Verhalten teilkristalliner Thermoplaste beim Lasersintern. Universität Essen, Dissertation. 2000

[6] Valko, E.I.C., C. K., 1965. Effects of Thermal Exposure on the Physicochemical Properties of Polyamides. Journal of Applied Polymer Science 9, 2855 - 2877.

[7] Rietzel, D., Kühnlein, F., Drummer, D., 2009. Selektives Lasersintern von teilkristallinen Thermoplasten. In: Tagungsband - Fachtagung Additive Fertigung pp. 57-71.

[8] Ehrenstein, G.W., Pongratz, S., 2007. Beständigkeit von Kunststoffen. Hanser Fachbuch. - ISBN 3446218513

[9] Allen, N.S., 1984. Thermal and photo-chemical oxidation of nylon 6,6: Some aspects of the importance of α,β-unsaturated carbonyl groups and hydroperoxides In: Polymer Degradation and Stability 8.

[10] Pongratz, S., 2000. Alterung von Kunststoffen während der Verarbeitung und im Gebrauch. , p. 79.

[11] Griskey, R.G., Lee, B.I., 1966. Thermally induced solid-state polymerization in nylon 66. In: Journal of Applied Polymer Science 10 , pp. 105-111.

[12] Gaymans, R.J., Amirtharaj, J., Kamp, H., 1982. Nylon 6 polymerization in the solid state. In: Journal of Applied Polymer Science 27 , pp. 2513-2526.

[13] Kühnlein, F., Drummer, D., Rietzel, D., Seefried, A., 2010. Degradation behavior and material properties of PA12-plastic powders processed by powder based additive manufacturing technologies., 3rd International Conference on Additive Technologies; DAAAM Specialized Conference, Nova Gorica, Slovenia, 2010.

[14] Drummer, D., Kühnlein, F., Meister, S., Drexler, M., 2012. Investigations on the degradation behaviour of PA 12 plastic pwoders - influence of high temperatures on the molecular weight, 13 th Annual International RAPDASA 2012 Conference South Africa, 2012.

[15] Wudy, K., Drummer, D., Kühnlein, F., Drexler, M., 2013. Influence of degradation behaviour of polyamide 12 powders in laser sintering process on produced parts, PPS-29, Nuernberg, 2013.

[16] Gornet, T.J., Davis, K.R., Starr, T.L., Mulloy, K.M., 2002. Characterization of selective laser sintering materials to determine process stability, Proceedings of the 13th International Solid freeform fabrication symposium 2002, Austin, Texas, 2002, pp. 546-553.

[17] Dotchev, K., Yusoff, W., 2009. Recycling of polyamide 12 based powders in the laser sintering process. In: Rapid Prototyping Journal 15 , p. 192 - 203.

[18] Wendel, B., Dallner, C., Schmachtenberg, E., 2008. Additive processing - New materials for fused deposition modelling Technical Papers, Regional Technical Conference - Society of Plastics Engineers 2008, pp. 693-697.

[19] Kruth, J.P., Levy, G., Klocke, F., Childs, T.H.C., 2007. Consolidation phenomena in laser and powder-bed based layered manufacturing. In: CIRP Annals - Manufacturing Technology 56, pp. 730-759.

[20] Pham, D.T., Dotchev, K.D., Yusoff, W.A.Y., 2008. Deterioration of polyamide powder properties in the laser sintering process, in "*Proceedings of the Institution of Mechanical Engineers" -- Part C* – In: Journal of Mechanical Engineering Science 222 , pp. 2163 - 2176.

[21] Rietzel, D., 2011. Werkstoffverhalten und Prozessanalyse beim Laser-Sintern von Thermoplasten. Universität Erlangen, Dissertation. 2011