Characterisation of the thermal ageing effects on the mechanical properties when reusing polyamide 12 in the selective laser sintering process

Charakterisierung der Auswirkungen thermischer Alterung auf die mechanischen Eigenschaften bei der Wiederverwendung von Polyamid 12 im selektiven Lasersintern

P. du Maire[1], E. Sert[1], M. Deckert[1], M. Johlitz[2], A. Öchsner[1]

Additive manufacturing is one of the key technologies for the future production of complex and individualised components. One of the most challenging questions to minimize the production cost is the reuse of the powder leftover after the building process. This study investigates the influence on the mechanical properties when reusing the leftover powder out of the process chamber up to four times. Tensile test specimens are produced and investigated. The results show a decreasing in the ultimate tensile strength with repeated reuse of the leftover powder. After four times of reuse the strength increases again. This cannot be explained by the literature and has to be verified in further investigations. The investigations reveal a high mechanical anisotropy as the strength highly depends on the component orientation in the process chamber. The particle shape does not show any differences between virgin and aged powder under the scanning electron microscope.

Keywords: Thermal ageing **/** powder recycling **/** selective laser sintering **/** polyamide 12 **/** mechanical properties

Die additive Fertigung zählt zu den Schlüsseltechnologien für die zukünftige Produktion komplexer und individualisierter Bauteile. Eine der größten Herausforderungen, um die Produktionskosten zu minimieren, ist die Wiederverwendung des nach dem Bauprozess übrig gebliebenen Pulvers. In dieser Studie wird der Einfluss auf die mechanischen Eigenschaften bei mehrmaliger Wiederverwendung des nicht aufgeschmolzenen Pulvers untersucht. Es werden Zugproben hergestellt und untersucht. Die Ergebnisse zeigen eine Abnahme der Zugfestigkeit bei wiederholter Wiederverwendung des Restpulvers. Nach viermaliger Wiederverwendung steigt die Festigkeit wieder an. Der Anstieg lässt sich nicht abschließend begründen und muss in weiteren Untersuchungen verifiziert werden. Die Untersuchungen zeigen eine hohe Anisotropie, da die Festigkeit stark von der Orientierung der Komponenten in der Prozesskammer abhängt. Unter dem Rasterelektronenmikroskop können keine Unterschiede zwischen Neupulver und thermisch belasteten Pulver festgestellt werden.

[1] Esslingen University of Applied Sciences, Faculty of Mechanical and Systems Engineering, Kanalstraße 33, Esslingen, Germany

[2] Univeristät der Bundeswehr München, Aerospace Engineering, Neubiberg, Germany

Corresponding author: P. du Maire, Esslingen University of Applied Sciences, Faculty of Mechanical and Systems Engineering, Kanalstraße 33, 73728, Esslingen, Germany,
E-Mail: philippe.du-maire@hs-esslingen.de

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1 Introduction

Additive manufacturing processes have already been in use for over 25 years in the field of prototyping (rapid prototyping) in industry and research [1]. Due to the increasing need of individualised products, as well as the possibility of producing complex geometries and the integration of functions, additive manufacturing in series production is one of the key technologies of the future [2]. In the area of polymer production selective laser sintering is one of the additive manufacturing processes that is currently at the transition stage from prototype tooling to series production [1–4]. For this reason, the selective laser sintering process is particularly important in the generative production of plastics [5].

Even though the selective laser sintering has become highly important for the future of plastic production, there is only a rather small amount of polymer materials, which are currently used in industries [1, 6]. A part from some exceptions like polypropylene and polyetheretherketone for special application, most of the currently used materials for selective laser sintering are based on the semi-crystalline thermoplastic polyamide like polyamide 11 and polyamide 12 [1–3, 6, 7]. It is estimated that 95 % of the polymer powder used in industries is based on polyamide 12, which further underlines the predominating market position of the polyamides [1].

In the selective laser sintering process, plastic powder is used as base material to manufacture the parts. The powder is successively applied in thin layers to a construction area, the so-called part bed and then melted locally with the help of a carbon dioxide laser. The molten polymer powder then solidifies and forms the layer fragments of the component. After the melt is solidified, the powder bed is lowered by one layer thickness, new powder is applied and the next layer is produced and bonded to its surroundings by repeated melting and solidifying of the new applied powder [8]. This process is then repeated until a new component is produced, layer by layer.

In order to reduce the warpage caused by fast cooling and to minimize the required laser energy so that only a small temperature increase is necessary to melt the plastic, the powder is preheated and set to a temperature just below the melting temperature [2, 9, 10]. This is achieved with the help of process chamber heaters. These high temperatures in the process chamber (around 175 °C for polyamide 12) lead to a thermal ageing of the unsintered powder, which results in a limited reusability.

This study aims to evaluate the effects of thermal ageing on the mechanical properties of samples made of polyamide 12 powder. For the investigations tensile test specimens are produced with different powder qualities in terms of their thermal ageing state and compared with each other. Mechanical properties of laser sintered parts have already been investigated by several authors [9, 11, 12]. These studies are carried out on virgin, aged and mixed powder and investigate different powder manufacturers or orientations in the build chamber, whereas the following study is more focused on the repeated use and hence the defined ageing of the base material. Additionally the morphology of the powder particles is analysed with the aid of a scanning electron microscope.

2 Methodology

The tensile test specimens are fabricated on a selective laser sinter system Vanguard HS from the company 3D-Systems Inc. equipped with a 100 W carbon dioxide laser. For the investigation in this study, a build volume of $380 \times 330 \times 275\ mm^3$ is used. As polyamide 12 is mostly used in industries, the samples are built out of the polyamide DuraForm PA from the manufacturer 3D-Systems Inc. The dimensions of the specimens are chosen according to DIN EN ISO 527-2 Type 1 A, *Table 1*.

In order to investigate the effects of different ageing states of the powder material, the samples are fabricated in several process cycles. A first production cycle is performed using only virgin pow-

Table 1. Dimensions of tensile test specimen (DIN EN ISO 527-2 Type 1 A).

Tabelle 1. Abmessungen der Zugproben (DIN EN ISO 527-2 Type 1 A).

l_1 [mm]	l_2 [mm]	l_3 [mm]	b_1 [mm]	b_2 [mm]	h [mm]
80	110	170	10	20	5

der. In the next step, the leftover powder in the building chamber is reused to fabricate another sample set. For the following production cycles only the left over powder is used, there is no addition of virgin or other powder material. This guarantees a defined thermal ageing, as the process parameter are kept the same. To ensure a clear investigation and a proper dataset this process is repeated four times. At the end there will be one set off tensile test specimens built with virgin powder and four sets produced with up to four times reused powder. Additionally, one set of test specimens is produced with a powder mixture of 60 % used powder and 40 % virgin powder, which is a common refreshing rate used in industries. In each building process, ten tensile test specimens were fabricated. Five samples were placed along the x-direction, parallel to the application direction of the powder and five along the y-direction, which is perpendicular to that, *Figure 1*. In order to produce the components, a layer thickness of 100 µm is chosen. Each built starts with a warm up layer of 12.5 mm total powder height, followed by a base layer of 2 mm and ends with a cool down layer of 2.54 mm. All tensile test specimens were fabricated at a process chamber temperature of 177 °C.

To characterize the changes in the mechanical properties of the components, the specimens are investigated regarding their tensile strength with the aid of a Zwick 1445–02, 10 kN universal testing machine. In order to obtain accurate values for the strains a modular sensor arm extensometer is used, *Figure 2*. At least three specimens are tested for each building direction and construction process to receive a clear assessment of the mechanical properties. The other samples are made as reserve in the case of an invalid test run. Furthermore, the morphology of the powder grains is investigated, using a Schottky field emission scanning electron microscope JSM-7200F from the manufacturer Jeol GmbH. As polyamide is a non-conductive material, a sputtering of the powder is required for the investigation. To realise the microscopy the samples are prepared with a thin sputter coating of gold. The applied gold serves as conductive layer without in-

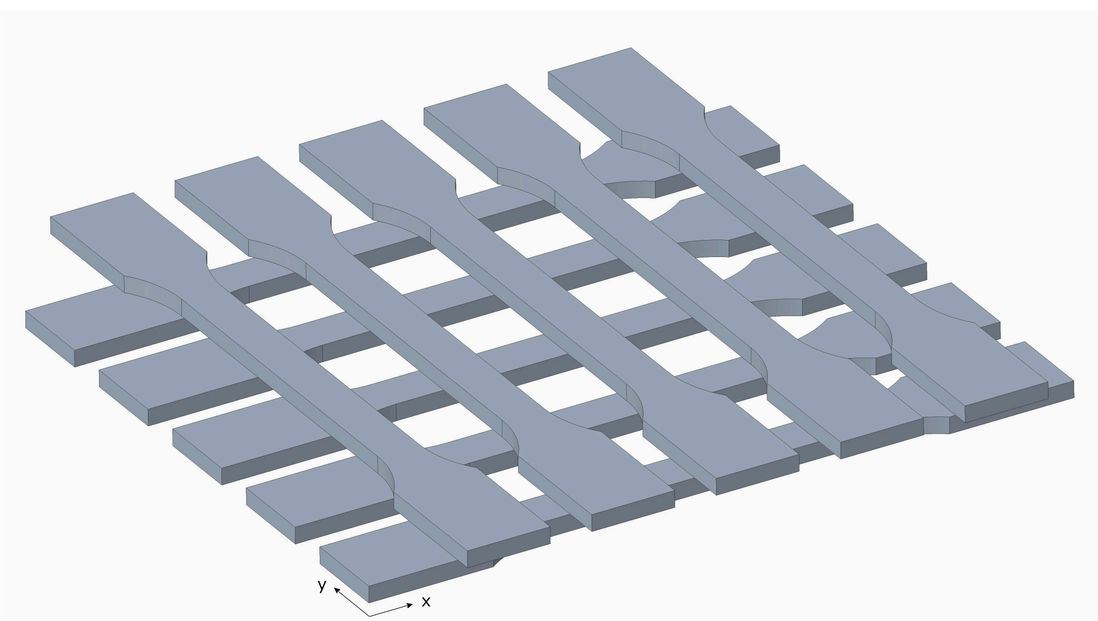

Figure 1. Orientation of the tensile test specimens in the process chamber.

Bild 1. Orientierung der Zugproben im Bauraum.

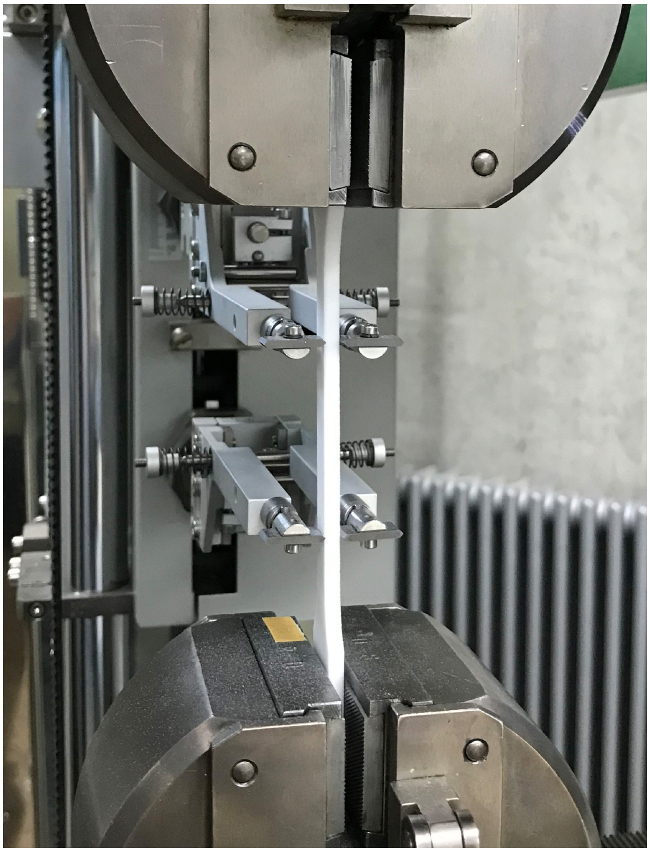

Figure 2. Specimen holder with sensor arm extensometer.

Bild 2. Probenhalter mit Fühler-Extensometer.

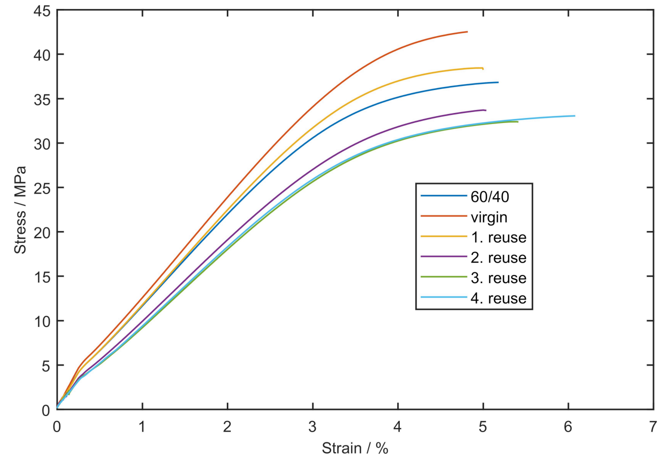

Figure 3. Stress-strain curves for tensile test specimens positioned along the powder application direction (x-direction).

Bild 3. Spannungs-Dehnungs-Diagramm für Zugproben, die entlang der Pulverauftragsrichtung (x-Richtung) angeordnet sind.

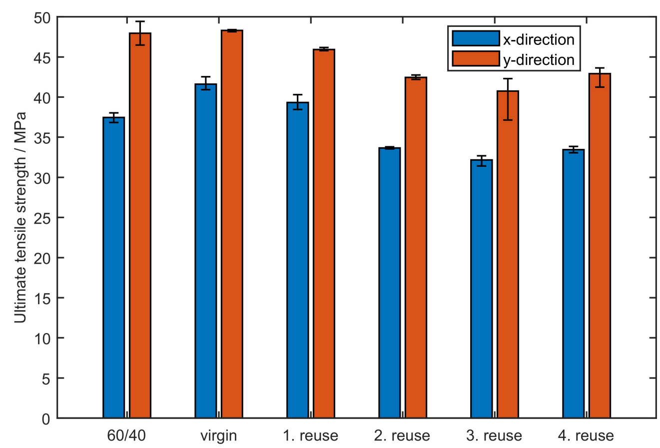

Figure 4. Ultimate tensile strength data for different thermal ageing states of the base material.

Bild 4. Zugfestigkeiten für unterschiedliche thermische Alterungszustände des Grundwerkstoffs.

fluencing the morphology of the grains, as its thickness is only in the range of 10 nm–15 nm.

3 Results and discussion

Investigating the tensile strength of the samples at room temperature indicates a decrease in strength with increasing thermal ageing of the powder, *Figure 3*. The stress-strain curves show exemplarily the results of one testing sequence of the specimens build up along the x-direction. It is evident that the tensile strength of the specimen, produced with a 60/40 powder mixture is roughly in the middle of all results. The resulting ultimate tensile strength of 36.8 MPa differs only by 0.6 MPa from the overall median (37.4 MPa), Figure 3. For components, fabricated perpendicular to the direction of the powder application (y-direction) the reached ultimate tensile strength can be compared with components made out of virgin powder, *Figure 4*. It is striking that the tensile strength for specimens produced with the powder reused four times increases again, Figure 3. Evaluating the complete dataset confirms this behavior, Figure 4. The increase in the ultimate tensile strength for the fourth production cycle can be clearly seen also for components produced perpendicular to the powder application direction (y-direction). Although the test results were clear, this behaviour cannot be confirmed by the literature and must be verified in further test series.

Furthermore, the elongation at break (6.08 %) for the four times reused powder is clearly higher than the other entire specimen that lie around a value of 5 %, Figure 3. The same behavior is obtained for the specimens allocated along the y-direction. This indicates a decrease in stiffness, which is must also be verified in further test series as this cannot be confirmed in the literature.

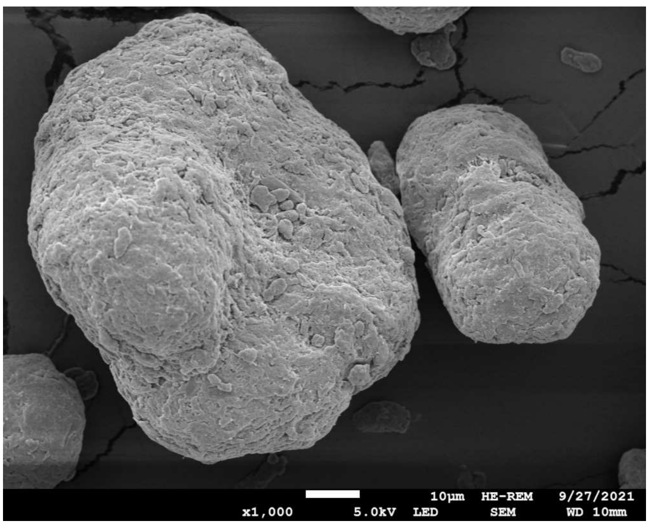

Figure 5. Scanning electron microscope images of the virgin powder.

Bild 5. Rasterelektronenmikroskopische Aufnahmen des Neupulvers.

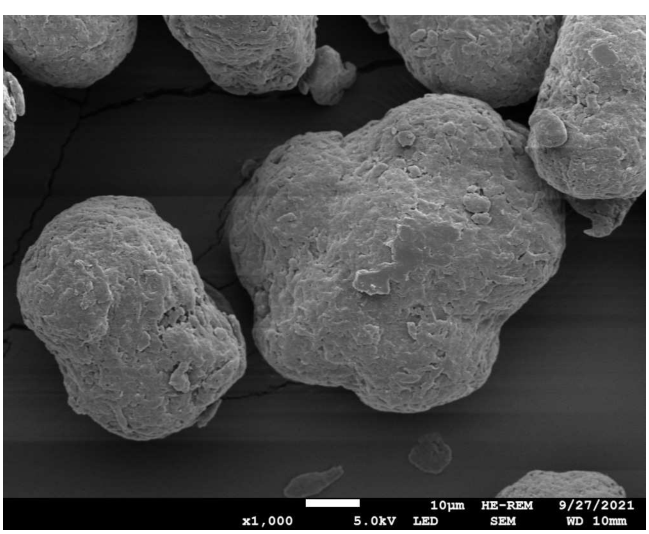

Figure 6. Scanning electron microscope images of the aged powder.

Bild 6. Rasterelektronenmikroskopische Aufnahmen des thermisch belasteten Pulvers.

Comparing the results for specimens fabricated in y-direction with those fabricated in x-direction shows that the ultimate tensile strength highly depends on the orientation in the process chamber, Figure 4. The strength increases in case of a specimen orientation along the y-direction in the mean by an average of 24 %, which underlines the importance of a proper component positioning for the manufacturing process. In the additive manufacturing, the mechanical anisotropy is a characteristic behavior and is confirmed by other studies [13, 14].

Contrary to expectations, no clear differences in the morphology of the virgin and the aged powder grains can be seen on the microscope images with a resolution of 1'000. At least a change in shape or particle size due to thermal degradation was expected. Both, the virgin and the aged powder exhibit the characteristic potato-like particle shape, *Figures 5, 6.* Since scanning electron microscope images only show a small section, further investigations should be carried out to obtain clear information about possible changes in particle size or distribution.

4 Conclusions

The investigated samples reveal a strong mechanical anisotropy. Tensile test specimens built perpendicular to the direction of the powder application show a significantly higher ultimate tensile strength compared to those fabricated along the direction of the powder application. When using a powder refreshing rate of 60 % aged powder and 40 % virgin powder the ultimate tensile strength of components positioned perpendicular to the powder application can be compared to the strength of components produced with virgin powder. This behavior cannot be confirmed for components produced along the powder application direction, where the strength are significantly lower. In general, a decrease in the ultimate tensile strength can be observed with repeated reuse of the leftover powder. This is the case for reusing the powder up to three times. Reusing the powder the fourth time results in an increase of the strength again, which could not be clarified finally and must be verified in further investigations. Analysing the powder particles with the aid of a scanning electron microscope did not show any changes of the morphology between virgin and aged powder. In order to obtain clear information about the effects on the powder particles, the particle size and particle size distribution should be further examined using laser diffraction.

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