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APPROACH TO DEFINING THE MAXIMUM FILLER PACKING VOLUME FRACTION IN LASER SINTERING ON THE EXAMPLE OF ALUMINUM-FILLED POLYAMIDE 12

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Abstract

Laser sintering is one of the most popular additive manufacturing techniques that uses thermoplastic polymer powders to generate layer-by-layer complex structures. Despite its broad application, some limitations exist restricting its further development. One such restriction is a narrow assortment of commercially available materials that would allow the production of the parts with the desired mechanical characteristics, which is the case with the widely used Polyamide 12 (PA12). Reinforcement of a matrix polymer with metal particles is routinely performed to achieve better mechanical properties. In this work, a PA12 system enhanced with a 35% volume ratio of aluminum was investigated. Mechanical characteristics, e.g. elastic and flexural moduli, were examined with respect to variation of manufacturing process parameters. In addition, a new methodology was tested, which should help determine the maximum filler packing volume fraction corresponding to the highest mechanical characteristics of a polymer-filler mixture.

Keywords

Maximum filler volume packing fraction, Laser sintering, Polymers, Reinforcement, Fillers, Additive manufacturing

Introduction

Additive manufacturing (AM) allows convenient generation of individual and complex structures by layers over a short time compared to conventional methods. This has contributed to the AM method's broad application in areas such as medicine or airspace [1]. Laser sintering (LS) is one such technique which has the capacity to develop into the manufacturing technology for small-series production. However, the main obstacle for that is the limited assortment of available materials. Compared to conventional manufacturing (CM), only several thermoplastic polymer powders, predominantly PA12, can be used in LS. As a result, final structures don't always have the desired mechanical characteristics [2].

Reinforcement of a polymer with diverse fillers is widely used to enhance material characteristics, and therefore the properties of the final product [3–5]. The type of filler, its shape and particle size distribution, as well as its material properties, all affect the properties of the final composite. In addition, the amount of the filler introduced is crucial for the mechanical properties [6]. Thus, it is vital to know the maximum amount of the filler that can be introduced to guarantee a favorable reinforcement of the material under examination.

Recent studies focused on the investigation of diverse fillers and filling ratios in LS [7–10]. Karevan et al. [7] investigated PA12 composites with two different mass fractions (wt%) of graphite nanoplatelets (GNP): 3 and 5 wt%. The results were compared with the same composites processed by injection molding (IM). The tests revealed that the best mechanical properties can be

achieved by introducing 3 wt% of GNP. Moreover, the choice of the processing method had almost no influence on the properties. Curling effect, which is known to occur in LS, was studied in detail by Mousa et al [8]. They investigated various PA12 compounds reinforced with 10, 20, 30, and 40 wt% of glass beads. They showed that the PA12 sample with 10 wt% of the filler demonstrated less tendency towards curling than other mixtures. Yan et al. [9] sintered PA12 filled with 30, 40, and 50 wt% of carbon fibers. They observed that the flexural characteristics improved with increasing the amount of the filler due to the good bonding between the carbon fibers and the PA12. Wudy et al. [10] studied various PA12 / glass beads blends and showed that the bonding to the matrix polymer dramatically decreased with a filler content of 50 vol% resulting in highly porous specimens.

In addition, there is no methodology or *Rule of Thumb* as to how much of the filler should be used in a LS process to guarantee the best properties. For this reason, estimation of the maximum filler packing fraction ($V_{f\,max}$) is important, because it will ideally allow rational use of resources and a much faster correct approximation of the filler quantity.

To the best of authors' knowledge, there are no methods that describe how the optimal filler content can be calculated for LS, and no research has been performed on this account. In this study, a potential approach to defining $V_{f\,max}$ in LS is described and was tested on aluminum-filled PA12 samples. Aluminum was selected as a filler because it effectively enhances mechanical properties of the final composite, is widely used for reinforcement in LS and inexpensive [3, 4]. Moreover, its use guarantees processability of our test compound in LS process. The chosen filler amount and its influence on the mechanical properties of the manufactured specimens were investigated while varying parameter combinations in the LS process.

Materials and Methods

Considering the excellent processability of commercially available aluminum-filled PA12 in LS and their good finishing properties [3, 4, 11, 12], aluminum powder (R&G Faserverbundwerkstoffe) and PA2201 (EOS) were chosen as the filler and matrix polymer for this study.

The maximum filler packing fraction ($V_{f\,max}$) can be obtained from the oil adsorption of a filler (O_A) using Equation 1, where ρ_f is the filler's density [6, 13]. The oil adsorption of aluminum was determined in conformity with DIN EN ISO 787-5 [14].

$$V_{f\,max} = \frac{1}{1 + \rho_f O_A / 100} \qquad \text{Equation 1}$$

It should be mentioned that $V_{f\,max}$ depends highly on the packing density (ρ_{pack}) of a matrix polymer, i.e. the higher the ρ_{pack} value is, the more filler could be mixed with it [6]. The particle form of the polymer powder and its further processing history define ρ_{pack}. Spherical particles represent the ideal case in which they could fill the space reaching the ideal theoretical packing density of 74%. For CM methods this value is typically close to 60%. Polymer powders that are commonly used in LS usually have ρ_{pack} in the range of 45 – 50% [2]. Thus, less filler amount is required to successfully reinforce a polymer in LS.

Our assumption was that in the ideal case a polymer with the ρ_{pack} value of 74% is able to completely accommodate $V_{f\,max}$ defined by Equation 1. Remembering that in the case of LS the filler content is lower, we used a direct proportion to describe $V_{f\,max}$ (Equation 2).

$$V_{f\,max\,LS} = \frac{\rho_{pack} \cdot V_{f\,max}}{74} \qquad \text{Equation 2}$$

To test this approach, it was supposed that PA12 has the ρ_{pack} of 50%, which is theoretically the maximum value among LS powders. This value would allow the best possible enhancement of material properties in LS. In practice, LS powders have packing density values lower than 50%. Therefore, a likely decline in the material characteristics should be expected when approaching this value due to excess of the filler [2, 6].

After determining $V_{f\,max\,LS}$ for aluminum (35%) according to Equation 2, the filler and the polymer were mixed using a TURBULA Shaker-Mixer (Willy A. Bachofen) for one hour at the nominal speed of 23 rpm. After that the LS processability of the collected mixture was verified by investigating flow and thermal characteristics of the material. The flow characteristics of the powder can be defined by measuring the bulk, and tapped densities, and also by calculating the Hausner ratio [2]. Polymer viscosity was studied by melt volume rate method (MVR) by loading the sample with 5 kg at 235°C, in accordance with DIN EN ISO 1133-1 [15]. The processing temperatures were determined by differential scanning calorimetry (DSC) under DIN EN ISO 11357-1 [16] using a Mettler Toledo calorimeter. The mentioned techniques allow to assess the processing capabilities of the mixed PA12 with 35 vol% of aluminum (further referred as PA12-35Al).

The next step was the fabrication of PA12-35Al specimens using a VanGuard HiQ HS machine (3D Systems). During the manufacturing process, various process parameters such as temperature (T), hatch distance (h), laser power (P) were examined and optimized. The layer thickness (d) and the laser speed (V_s) were kept constant at 0.1 mm and 10160 mm/s, respectively. The surface energy density (E_S) was calculated using Equation 3 [2]. All conducted experiments are listed in Table 1.

Table 1. The list of experiments and corresponding LS process parameters of PA12-35Al

Experiment	Temperature T, °C	Hatch distance h, mm	Surface Energy E_s, J/mm^2	Laser Power P, W
1	175	0.20	0.015	30.5
2			0.020	40.6
3			0.025	50.8
4		0.25	0.015	38.1
5			0.020	50.8
6			0.025	63.5
7		0.30	0.015	45.7
8			0.020	61.0
9			0.025	76.2
10	178	0.25	0.015	38.1
11			0.020	50.8
12			0.025	63.5
13	182	0.25	0.015	38.1
14			0.020	50.8
15			0.025	63.5

$$E_S = \frac{P}{h \cdot V_s}$$ Equation 3

After the manufacturing process, the sintered parts were examined with respect to their mechanical characteristics and how they depend from the processing parameters chosen. Density measurements of the solid bodies, tensile and bending tests were then carried out. The density values were calculated using the Archimedes' method and in accordance with DIN EN ISO 1183-1 [17]. For the tensile tests, five specimens from each parameter set were sintered in the *x*-direction. The tensile tests were conducted under DIN EN ISO 527-1 [18] with a testing speed of 5 mm/min using tension bars of Type A (DIN EN ISO 3167 [19]). For the bending tests, rectangular samples (L × W × H: 80 × 10 × 4 mm) were constructed and bent according to DIN EN ISO 178 with a bending speed of 10 mm/min [20].

Our experimental results were then compared with those of the commercially available aluminum-filled materials on the PA12 basis: Alumide (EOS) and DuraForm Prox AF+ (3D Systems). This would help us to draw conclusions about the applicability of our approach to defining $V_{f\,max\,LS}$.

Results and Discussion

Powder characteristics

First, flow and thermal characteristics of the powder were investigated to assess the processability of the prepared powder mixture. To evaluate the PA12-35Al powder properties, the pristine PA12 (PA2201, EOS) was used as a reference material and was additionally examined in the same manner as our test powder.

Good powder flowability is essential for efficient spreading of the powder across the building platform during the manufacturing process. To evaluate the flowability of our mixture, first the bulk and the tapped densities were determined, and from these the Hausner ratios were calculated (Table 2).

Table 2. The bulk and tapped densities as well as Hausner ratios of pure and aluminum-filled PA12

Material	Bulk density, g/ml	Tapped density, g/ml	Hausner ratio, -
PA12	0.456	0.493	1.08
PA12-35Al	0.652	0.739	1.13

It is important to know how good the powder particles fill the space in a defined volume, which can be examined by calculating the specific gravity of the powder under study. For that the densities of the solid bodies for both reference and composite materials have to be estimated. The experimentally obtained density of the pristine PA12 (ρ_m) was ~1.0 g/cm^3. The *target* density of the PA12 mixture with 35 vol% (V_f) of aluminum was calculated using Equation 4 and is 1.6 g/cm^3 [5]. The density of aluminum (ρ_f) was 2.7 g/cm^3 as specified by the manufacturer.

$$\rho = V_f \cdot \rho_f + (1 - V_f) \cdot \rho_m$$ Equation 4

Therefore, the specific gravities calculated were ~46% for the PA12 and ~41% for the PA12-35Al. Irregular-shaped particles of aluminum are the reason for the observed decreased value of the specific gravity, which results in less volume filling in the PA12-35Al mixture than in the

pristine PA12 powder [21]. As a consequence, more porosity is expected for the sintered parts [2, 21].

By comparing bulk and tapped densities, it is possible to acquire information about the powder flowability, and therefore derive the Hausner ratio, as we described above. In brief, the lower the ratio is, the better the flow characteristics of the powder are. In the case of PA12-35Al, the Hausner ratio slightly increased compared to PA12. Nevertheless, both values are in the range of good powder flowability, which should be under 1.25 according to Schmid et al. [2]. The ratios below this value should theoretically allow smooth powder spreading during the LS process.

Good binding between the fabricated layers is vital to achieve superior mechanical properties of the manufactured parts. For this reason, the polymer viscosity was investigated using MVR method. The obtained values for PA12 and PA12-35Al were 73 and 9 cm^3/10min, respectively. Proper melt formation is expected if the results are above 30 cm^3/10min [2]. The aluminum-filled polymer shows increased viscosity, hence decreased melt flowability.

Prior to the manufacturing process, the temperature window in which the processing can be executed has to be estimated. The crystallization temperature (T_c) and the melting point (T_m), as well as their onset values ($T_{c\ (onset)}$ and $T_{m\ (onset)}$) were determined using DSC analysis, with the results presented in Figure 1. Good processability is typically observed between the onset values. The determined processing range of both materials is similar, with the PA12 sample showing the $T_{c\ (onset)}$ and $T_{m\ (onset)}$ values at 152.2 and 181.9 °C, and the PA12-35Al at 152.2 and 180.9 °C, respectively. Therefore, the processing range of both materials is ~30 K.

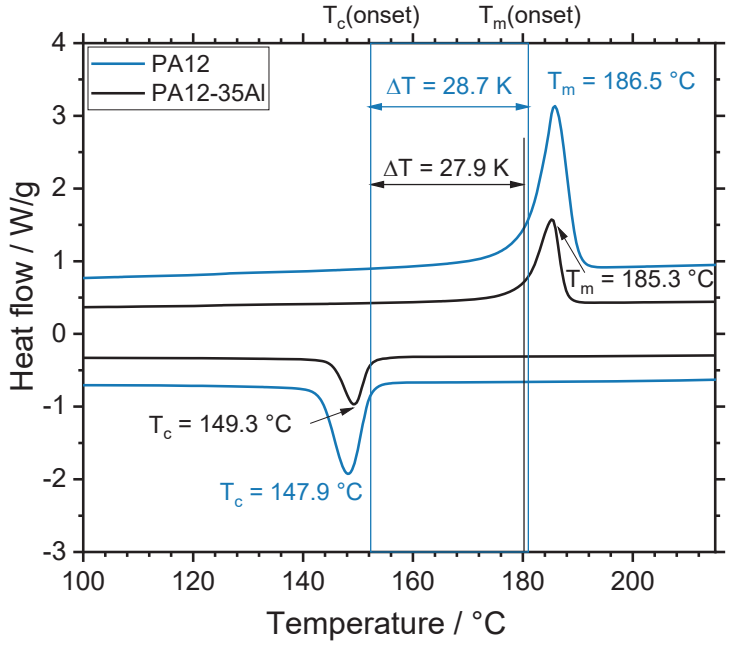

Figure 1. Crystallization and melting behavior of PA12 and PA12-35Al

Based on the acquired results of the flow and thermal characteristics, the PA12-35Al appears processable in the LS. However, the high viscosity might be an obstacle in producing good-quality parts.

Laser sintering and the mechanical characteristics of the manufactured parts

The PA12-35Al proved to be not difficult to process. The spreading of the powder across the building area was smooth and homogenous, while the melting traces looked flat and slightly sunk in the powder bed. In general, the LS process of the PA12-35Al was similar to that of the

unblended PA12. A minor difference noticed is that the powder spreading was significantly smoother with increasing process temperature in the case of PA12-35Al.

The best melt formation, as well as sufficient layer binding, can be expected if the samples show high densities [2], and the higher density is, the better the mechanical properties of the manufactured samples are. The density values of all manufactured samples (Table 1) are shown in Figure 2.

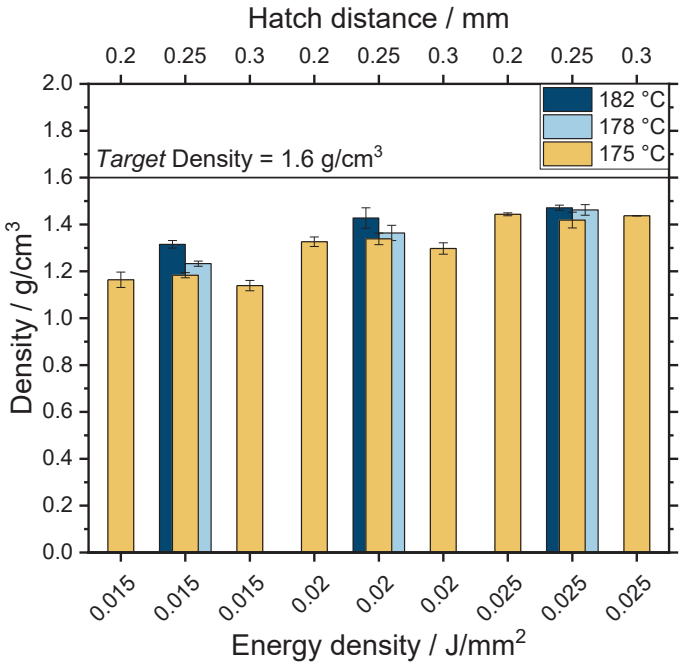

Figure 2. The density of the sintered parts depending on various process parameters and temperatures

According to the experimental results of the parts manufactured at 175 °C (Figure 2), the density of the samples increases with decreasing hatch distance and increasing energy density. Parts sintered with the same energy density and different hatch distances showed almost no differences in the density values. The samples with a hatch distance of 0.15 mm showed some deformation, while a hatch distance of 0.3 mm resulted in smaller density values. Therefore, only a hatch distance of 0.25 mm was further investigated at higher temperatures (178 and 182 °C). We observed that at 182 °C, an energy density of 0.025 J/mm^2, and a hatch distance of 0.25 mm the highest density of 1.47 g/cm^3 was reached, which constituted ~92% of the *target* density value (1.6 g/cm^3).

According to the manufacturing data of EOS and 3D Systems, their aluminum-filled materials based on PA12 have densities of 1.36 and 1.31 g/cm^3, respectively, albeit the exact filler content isn't known [3, 4]. However, the approximate amount of the filler in these materials could be estimated by using Equation 4 and inserting the known densities of aluminum (2.7 g/cm^3) and PA12 (1.0 g/cm^3). The calculated V_f of aluminum in aluminum-filled materials of EOS and 3D Systems is ~21 and ~18 vol%, respectively. Therefore, the highest content of aluminum in the tested PA12-35Al can be confirmed.

The mechanical properties were examined by performing tensile and bending tests on the parts, which were printed in the *x* direction. The results of the tensile tests are presented in Figure 3 and the results of flexural modulus and flexural strength are shown in Figure 4.

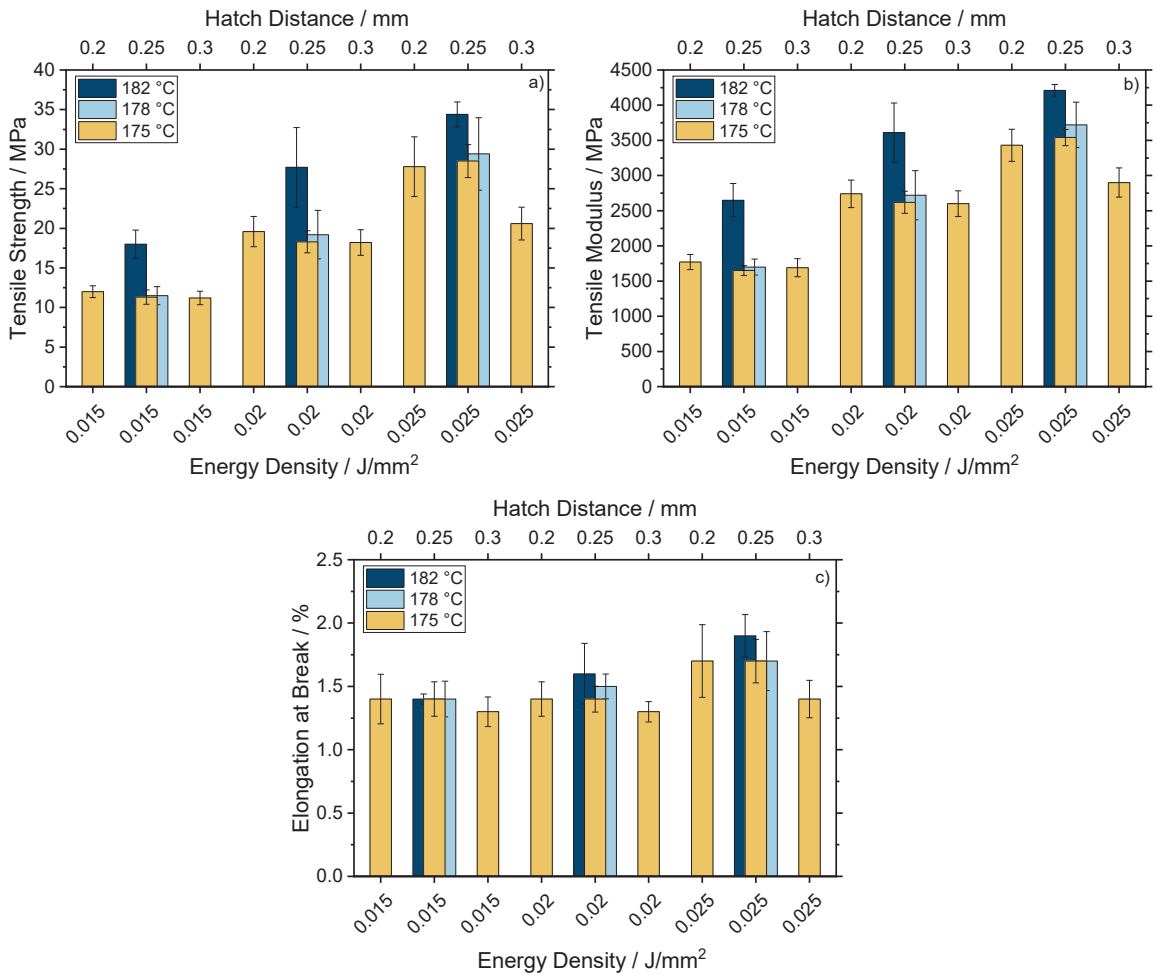

Figure 3. Tensile strength (a), tensile modulus (b) and elongation at break (c) of the PA12-35Al samples sintered according to Table 1

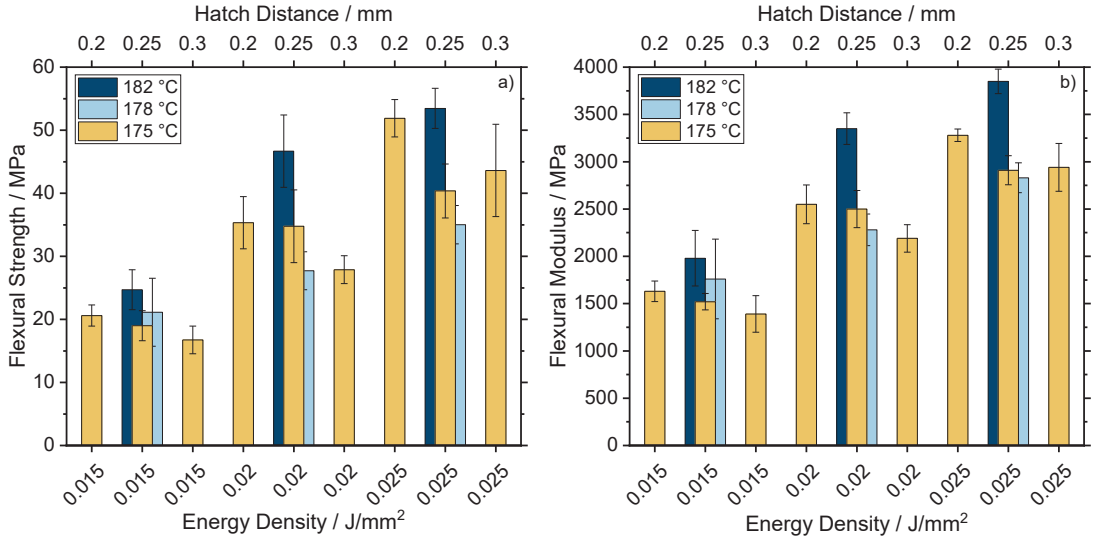

Figure 4. Flexural strength (a) and flexural modulus (b) of the PA12-35Al samples sintered according to Table 1

The same tendency as with the density measurements was observed here. More specifically, the better mechanical properties were observed with increasing temperatures and energy densities while decreasing hatch distances. For instance, a slight improvement of ~5% in tensile modulus and tensile strength was observed with decreasing hatch distance or increasing process temperature from 175 to 178 °C. By further increasing temperature to 182 °C, the tensile characteristics were found to significantly improve up to 40% in comparison to the samples manufactured at 175 °C. Among all specimens the elongation at break was approximately 1.5%, which is rather too low for the thermoplastic polymers and points to the rigidness and brittle behavior of the manufactured samples [22]. However, such behaviour is common among the reinforced polymers which have significant losses in elongation at break due to the introduction of a filler [22, 23].

With decreasing hatch distance both flexural strength and flexural modulus increased up to 20 and 15%, respectively. The samples sintered at 182 °C demonstrated a further enhancement in flexural properties up to 25%.

The maximum tensile and flexural moduli of the specimens were observed at an energy density of 0.025 J/mm^2, a hatch distance of 0.25 mm, and at 182 °C. The maximum values of tensile and flexural moduli were 4210 and 3850 MPa, respectively. These values are ~60% higher than that of the samples processed at a lower energy density of 0.015 J/mm^2 and at 175 °C.

The commercially available aluminum-filled materials from EOS and 3D Systems demonstrate slightly improved flexural and tensile characteristics (Table 3), though the filler content is supposed to be lower than in the investigated PA12-35Al. This means that anticipated enhancement of mechanical properties didn't occur. On the one hand, the reason could be the low adhesion between PA12 and aluminum powder since the latter wasn't surface-treated which guarantees superior bonding between filler and polymer particles [6]. On the other hand, the chosen filler quantity introduced into the polymer matrix could be too high, therefore resulting in less than optimal coverage of the filler by the polymer [6].

Table 3. Mechanical characteristics of commercially available aluminum-filled PA12 [3, 4]

Material	Tensile Modulus, MPa	Tensile Strength, MPa	Elongation at break, %	Flexural Modulus, MPa	Flexural Strength, MPa
Alumide (EOS)	3800	48	4	3600	72
DuraForm Prox AF+ (3D Systems)	4340	37	3	3710	64

Conclusions

The new approach of defining the maximum filler packing fraction in the polymer system for the laser sintering was tested. Due to good processability of the commercial aluminum-filled powders, PA12 and aluminum were chosen as a matrix polymer and a filler for the test compound. Of importance was to verify the applicability of the proposed approach by examining mechanical properties of sintered specimens. The results of the performed mechanical tests showed that the tested filler amount of 35 vol% proved to be above the limit where no enhancement in properties can be expected. This can be also observed by comparing mechanical characteristics of PA12-35AL with aluminum-filled materials from EOS and 3D Systems, both of which supposedly have less aluminum incorporated in the PA12. The experimentally determined density values of PA12-35Al were ~8% lower than the target value of 1.6 g/cm^3, which might indicate the presence of some

aluminum particles that are not completely bonded to the melted polymer, therefore resulting in porous and brittle structures. As a result, no enhancement was observed in the tested samples.

The observed decline of the mechanical properties was taken into consideration by assuming the initial packing density of PA12 with a maximum value of 50%. Therefore, the proposed and tested approach based on estimating the optimal filler volume packing fraction for laser sintering can be considered viable. However, a further testing of different filler ratios is needed in order to correlate them with the actual packing density of a polymer.

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