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Powder bed fusion of ultra-high molecular weight polyethylene using ultra-short laser pulses

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Abstract

Laser powder bed fusion (L-PBF) of ultra-high molecular weight polyethylene (UHMWPE) is a new approach to fabricate complex components for medical implants. CO\textsubscript{2} laser radiation is the method of choice to selectively heat up the powder particles above the melting point. Although previous studies have shown the feasibility to fuse UHMWPE, the produced specimen lack of warping and degradation. Moreover, the achievable geometrical resolution is limited by the large spot size of several 100 µm. In this paper, we demonstrate an alternative approach for L-PBF of UHMWPE by using 500 fs laser pulses at a wavelength of 1030 nm. The peak intensity of several 100 MW/cm\textsuperscript{2} allows for efficient multi-photon absorption in the transparent polymer. Thus, it was possible to completely melt the powder with less degradation. Furthermore, the achieved tensile strength of 4 MPa is 60 % higher in comparison to produced samples using conventional CO\textsubscript{2} L-PBF.

Keywords: Laser powder bed fusion; Additive manufacturing; Selective laser sintering; UHMWPE; Ultrashort laser pulses

1. Introduction

Laser powder bed fusion (L-PBF) enables the consolidation of polymer powder particles without the need for high pressures and reaction times [1]. The choice of polymers suited for L-PBF is limited, since potential

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candidates need to fulfill a whole range of powder- as well as material related properties to be able to be processed [2]. For applications as medical implants, UHMWPE has promising physical properties such as high abrasion and impact resistance, self-lubrication and high chemical stability [3-5]. However, an important drawback is the extremely high viscosity of the melt of up to $10^{10}$ Pa·s, which impedes common polymer processing routes of melt injection molding with screw extruders [6-8]. In this way, UHMWPE components such as artificial joint replacements are manufactured by ram extrusion or compression molding followed by various post-processing steps to bring the parts into the desired shape. In contrast to that, additive manufacturing by L-PBF offers the opportunity to fabricate e.g. tailor-made implants for medical applications. Due to the low linear absorption coefficient of UHMWPE of 0.01 cm$^{-1}$ [9] in the near infrared wavelength range, continuous wave (cw) fiber and Nd:YAG lasers are not suitable to deposit enough energy for localized melting. For this purpose, CO$_2$ lasers at a wavelength of 10.6 µm [10-12] are used for the laser sintering of polymeric materials [13, 14]. In recent years, first investigations have been carried out to fuse UHMWPE particles with CO$_2$ lasers [15]. The produced parts are warped or shrunken with a size deviation of 2-8 % and the mechanical properties are significantly worse than conventionally molded UHMWPE [16, 17].

In contrast to cw radiation, focused ultra-short laser pulses (USP’s) with pulse durations in the femtosecond range deliver peak intensities that are several orders of magnitudes higher. Therefore, nonlinear laser-matter interactions increase the number of free-carriers in transparent materials for an enhanced absorption [18-20]. This multi-photon excitation in the focal volume is already in use e.g. for the inscription of waveguides in glasses [21, 22] and to accumulate heat for local welding [23-25].

In this paper, the interaction of 500 fs pulses at a wavelength of 1030 µm with UHMWPE powder is investigated. For this purpose, scattering experiments using an integration sphere have been conducted to quantify the effect of the nonlinear absorption. Based on these results, L-PBF was realized by applying an average power of 30 W at a repetition rate of 10 MHz. Finally, the produced specimens were analyzed by their consolidation characteristics, crystallinity and tensile properties.

2. Experimental Design

2.1. Powder

The milky white UHMWPE powder used in the experiments is GUR® 4150-3 provided by Celanese. The SEM image in Fig. 1 (a) shows, that the particles have an ellipsoidal shape with a flocculent, nodular surface morphology.

![Image](image_url)

Fig. 1. (a) SEM image a representative powder particle; (b) Histogram and cumulated density of the powder particles obtained by laser diffraction analysis; (c) Optical microscopic image of a 150 µm thick powder layer spread on a glass substrate.
The powder has a monomodal distribution of particles with a mean diameter of 59 µm (D50) (Fig. 1 (b)). The distribution ranges from 28 µm (D10) to 99 µm (D90). The particles tend to agglomerate after recoating (Fig. 1 (c)), whereas layer thicknesses larger than 100 µm are needed for a sufficiently homogeneous spreading.

2.2. Z-Scan on polymer powder

The setup for measuring the nonlinear absorptance of the UHMWPE powder is shown in Fig. 2. Powder with a thickness of 4 mm is deposited and flattened on a diffuser in an integrating sphere (Newport, 819C-SF-4). Ultrashort laser pulses with a duration of 500 fs are focused with a 250 mm plano-convex lens in the powder bed. The resulting spot diameter d0 is 48 µm (Rayleigh length zR = 1.75 mm). The scattered laser signal of a single pulse is measured with the help of a photodiode PD2 (Thorlabs, DET10AM). Disturbing interferences by the laser induced plasma are removed by a narrow bandwidth filter at 1025 nm. The incidence angle of the laser beam was adjusted to 4° to reduce scattering losses through the entrance port. Pulse to pulse fluctuations are measured with PD1, which detects a small fraction of the laser signal reflected by a quartz wedge.

![Fig. 2. Schematic representation of the setup for measuring the nonlinear absorptance of the powder](image)

In this configuration the captured relative intensity of the scattered signal Q is the sum of the reflected R, scattered S and transmitted T part of the laser pulse. Thus, the total absorptance A of the powder is A = 1 − Q, which consists of a linear Alin and nonlinear Anl fraction. Finally, the z-scan is realized by shifting the position of the focusing lens with a translation stage. Assuming that there are no significant changes in R and S, the measured signal is analogous to the open aperture measurement of a conventional z-scan [27, 28]. For the evaluation, the maximum intensity I0 and pulse energy density (fluence) Φ of the laser pulses are used. Their correlation is given by Eq. 1:

\[
I_0 = \frac{9 E_P}{\pi d_S^2} \cdot \frac{1}{t_P} = \Phi \cdot \frac{1}{t_P} \tag{1}
\]

where EP is the pulse energy, dS is the beam diameter on the powder surface and tP is the pulse duration.

2.3. L-PBF setup

The L-PBF process was performed on an in-house built device, which is connected to a mode locked fiber laser system from Active Fiber Systems (Fig. 3). The laser emits pulses with a duration of 500 fs and a maximum repetition rate of 20 MHz. The maximum average power on the surface of the powder bed is 30 W. The
repetition rate and pulse energy are adjusted with an acousto-optical modulator (AOM). The pulse trains are scanned using a galvanometer scanner (SCANLAB, HurryScan II 14), which is equipped with a 163 mm F-theta. The resulting spot diameter of the focused pulses is 40 µm \((1/e^2)\). L-PBF inside the sealed chamber starts on a thick powder bed without direct connection to the build platform. After illumination, the build stage moves down by a specific layer thickness and a recoater wipes fresh powder from the reservoir to the processing zone followed by the next illumination. During the experiments the chamber is flooded with nitrogen to keep the oxygen level below 1%. Due to the low thermal conductivity of UHMWPE of 0.5 W/m·K \([29]\) the resolidification of the molten material takes several seconds. Thus, a dwell time of at least 60 s was programmed before the next powder layer was supplied.

![Diagram of the L-PBF setup](image)

Fig. 3. Scheme of the of used L-PBF setup

2.4. Characterization methods

The as-built surfaces of the fused and fractured specimens were analyzed using optical microscopy (Nikon Eclipse LV100) and scanning electron microscopy (SEM, LEO 1525 Gemini) at an accelerating voltage of 5 kV. The crystallinity was determined by confocal Raman spectroscopy (Renishaw inVia Raman Microscope) using a 5x objective (NA 0.1) at an excitation wavelength of 532 nm. Furthermore, tensile tests were performed with the universal testing machine Zwicki-Line Z.10 by ZwickRoell on samples complying to the EN ISO 527-2 1BB standard.

3. Results and Discussion

3.1. Nonlinear absorption

The results of the z-scan measurement as described in section 2.2. are exemplarily shown in Fig. 4 (a) for a maximum fluence \(\Phi_{\text{max}}\) of 0.25 J/cm\(^2\) \((I_{\text{max}} = 0.5 \text{ TW/cm}^2)\). The Q-curve is symmetric with respect to the z-axis. The linear absorbance \(A_{\text{lin}}\) of the 4 mm thick power bed is determined by the edges of the trace to 0.6 ± 0.3 %, which is independent on the applied fluence. The bandgap energy of UHMWPE is in the range of 1.8 eV \([30]\) and 3.25 eV \([31]\). Due to the photon energy of 1.2 eV (1030 nm) of the laser pulses, electronic excitation could be achieved either by two-photon (2PA)- or three-photon absorption (3PA) processes. The experimental data was fitted using the coupled analytical model for simultaneous 2PA and 3PA in comparison to the analytic models for pure 2PA and pure 3PA \([32, 33]\). The results confirm that the excitation of UHMWPE is not based
on pure 2PA. Instead the excitation can be described by either pure 3PA or even by simultaneous two and three photon absorption. This multi-photon absorption leads to a significant drop of the transmittance with a maximum nonlinear absorptance $A_{nl}$ of $5.5 \pm 0.5\%$, when the focus is located on the powder surface (highest fluence).

![Graph](image)

Fig. 4. (a) “Open aperture” related $z$-scan at a peak fluence of $\Phi = 0.25\ J/cm^2$ together with the fits of the models for pure 2PA (blue dashed curve), 3PA (green dotted/dashed curve) and simultaneous 2PA and 3PA (black solid line); (b) Maximum nonlinear absorptance in dependence on the peak fluence.

The peak values of $A_{nl}$ are continuously growing with increasing fluence (Fig. 4(b)). The curve reaches a saturation at approximately $0.4\ J/cm^2$ and a nonlinear absorptance of $6\%$. At higher fluences, the absorptance increasingly rises linear up to $0.8\ J/cm^2$. An excitation of the same position with a second pulse show an increased absorptance, which indicates a permanent chemical modification of UHMWPE. Damage and ablation of the powder takes place by exceeding a fluence of $0.8\ J/cm^2$. In this regime shockwave expansion and particle removal is observed.

The absorptance characteristics are changing by irradiating the powder with multiple pulses as shown in Fig. 5. At an average power of $30\ W$ and high repetition rates of $20\ MHz$ and $5\ MHz$, i.e. at fluences of $0.06\ J/cm^2$ and $0.24\ J/cm^2$, the particular curves reach absorptance levels comparable to the single pulse excitation (see Fig. 4(b)) and show a constant course over the exposure time, which indicates a full relaxation of the particles even after a short laser-off-time of $50\ ns$ ($20\ MHz$).
Fig. 5. (a) Time resolved measurement of the nonlinear absorptance for different repetition rates at constant average power of 30 W and a spot diameter of 80 µm; (b) Nonlinear absorptance after a particular number of applied pulses for a constant fluence of 0.4 J/cm² and different repetition rates

A significant change of the absorptance during the repeated excitation is observed at 3 MHz and 0.4 J/cm² that is close to the threshold for permanent modifications using single pulses. The accumulative effect of the pulse train results in an increased absorptance up to a maximum value of 25%. At a repetition rate of 2 MHz (0.6 J/cm²) the absorptance increases more rapidly and achieves a peak value of around 50% but at the same time leading to excessive ablation and blasting of the particles that need to be avoided in laser powder bed fusion. Below the ablation threshold, a repetition rate above 100 kHz is needed for a significant change of the absorptance to enable a sufficient heat accumulation (see Fig. 5 (b)).

3.2. Powder bed fusion

The previous investigations show, that 500 fs pulses enable a sufficient energy transfer to UHMWPE controlled by laser fluence and repetition rate. On that basis, L-PBF was performed at an average power of 30 W and a repetition rate of 10 MHz. With a focal diameter of 40 µm, the resulting fluence was 0.47 J/cm². Single areas with a size of 2 x 2 mm² were scanned, whereas the scan speed v as well as the hatch spacing h were varied from 100 mm/s to 500 mm/s and 15 µm to 100 µm, respectively. The specific energy density $E_S$ was used to correlate the different parameters with the consolidation characteristics, as given by Eq. 2 [10]:

$$E_S = \frac{P_{av}}{v \cdot h}$$

Four different consolidation regimes could be classified as shown in Fig. 6 (a). At energy densities of more than 9 J/mm², complete melting leads to a smooth and closed surface (Fig 6 (b) i, red region). After that, a transition from partial melting (ii, yellow region) to particle neck sintering (iii, green region) could be observed at energy densities down to 5 J/mm². Below 4 J/cm² the powder particles are weakly connected to each other (iv, cyan region).
Fig. 6. (a) SEM images (top view) produced using different energy densities; (b) Correlation between different consolidation characteristics in dependence of the scan speed and hatch spacing.

The boundaries of the consolidation regimes are separated by the iso-lines of the specific energy densities (see Fig. 6(b)), which indicates that the scanning time per unit area is a decisive factor for a sufficient accumulation of heat to control the fusion process.

3.3. Crystallinity

The mechanical performance of UHMWPE is influenced by the crystalline structure and oxidation state [50]. These features can be determined by measuring the Raman spectrum within the range of 1000 - 1500 \( \text{cm}^{-1} \) (Fig. 7(a)). The different vibrational, twisting and bending modes can be allocated to amorphous and crystalline features [34, 35, 36].

The volume fraction of the crystalline \( \alpha_c \) and amorphous phases \( \alpha_a \) as well as the oxidation index (OI) are determined using Eq. 3-5 [34, 35, 36]:

\[
\alpha_c = \frac{I_{1293}}{I_{1293} + I_{1305}}
\]
\[
\alpha_a = \frac{I_{1080}}{I_{1293} + I_{1305}} \\
OI = \exp\left\{1.19 \tan\left[14.26 \left(\frac{I_{1414}}{I_{1293} + I_{1305}}\right) - 0.26\right] - 0.13\right\}
\]

where \( I_x \) are the baseline corrected integrated band intensities. The estimated crystallinity of the untreated powder is \( 78 \pm 2 \% \) (see Fig. 7 (b)) that is in good agreement with literature (70-75 \%) [37]. After laser excitation the crystallinity is decreasing with increasing specific energy density down to 50 \% at 6 J/mm\(^2\) in the sintering/melting regime, which is comparable to extruded and manufactured UHMWPE implants [36, 38]. By exceeding the threshold to realize complete melting, the crystallinity drops to 35 \%. The increasing amorphousness at around 6 J/mm\(^2\) can be attributed to enhanced cross-linking of adjacent polymer chains [39].

The oxidation index gives important information about oxidation reactions and degradation of the polymer [Meh19 38]. It follows the same trend as the amorphous phase in dependence on \( E_s \). The OI value of the powder is 1.5 ± 0.1 and therefore much higher than that of the adhered (0.15), sintered (0.2) and molten (> 0.3) material. This could be the result of aging effects of the powder stored in air. It is considered that an OI value of 3 represents the threshold to the degradation of mechanical properties. This threshold is not exceeded within the scope of our investigated processing parameters, but a clear tendency of higher oxygen degradation with increasing heat load is recognizable.

3.4. Tensile properties

For the preparation of test bars, an optimal processing regime with a scan speed of 150 mm/s and a hatch spacing of 30 \( \mu \)m at an average power of 30 W (6.7 J/cm\(^2\)) was used (see Fig. 8 (a)). The bars were built lying horizontally in the powder using a layer thickness of 500 \( \mu \)m. To overcome warping and roll-up of the fused layers, the whole area was separated in 6 islands with an overlap of 200 \( \mu \)m. The produced specimens have a total height of 2.5 mm and show a color change in the overlapping zone as a result of the double exposure.

![Fig. 8. (a) Tensile test specimen according to the EN ISO 527-2 1BB standard are separated in single islands; (b) Strain-stress diagram of different samples produced with the same processing parameters](image)

The “as-built” shapes are in an acceptable range for this study with deviations of less than 100 \( \mu \)m in lateral direction and 300 \( \mu \)m in vertical direction.
The stress-strain diagram of five samples is shown in Fig. 8 (b). The average ultimate tensile strength (UTS) is 3.9 ± 0.3 MPa, which is 60 % higher than in previous research on laser sintering of UHMWPE (2.4 ± 0.2 MPa [40]), but only approximately 8 % of the UTS of compression molded UHMWPE [41]. The Young modulus is 45.3 ± 28 MPa, which is the same range as reported for laser sintered UHMWPE [40], but only about 5 % that of classically prepared UHMWPE samples (0.9 GPa [42]). The elongation at break is 8.6 ± 3.3 %, which is lower than that of laser sintered UHMWPE of the previous study (51 % [40]) and way lower than that of classically prepared UHMWPE samples with values up to 525 % [42].

4. Conclusion

Ultrashort laser pulses enable the excitation of UHMWPE via multi-photon absorption. By adapting the pulse repetition rate, significant heat could be accumulated in the illuminated powder volume. With this method, we demonstrated the feasibility of laser powder bed fusion using pulses with a duration of 500 fs to achieve complete selective melting of UHMWPE powder at an average power of 30 W, repetition rate of 10 MHz and specific energy densities above 6 J/mm². Warping effects could be minimized by separating the area in islands of less than 4 x 4 mm². The shape deviation of the produced parts using a layer height of 500 µm is around 100 µm. The achieved crystallinity of the molten polymer is higher than 50 %, which is in good agreement with conventional molded UHMWPE and the ultimate tensile strength is 3.9 ± 0.3 MPa. This value is 60 % higher in comparison to previous approaches in laser sintering with CO₂ lasers, enhancing the potential for part building in additive manufacturing of UHMWPE.

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References


