Material and process engineering aspects to improve the quality of the bonding layer in a laser-assisted fused filament fabrication process

Gerhard Bräuer *, Klaus Sachsenhofer, Reinhold W. Lang

Institute of Polymeric Materials and Testing, Johannes Kepler University Linz, Altenberger Strasse 69, 4040 Linz, Austria

ABSTRACT

The mechanical properties of components manufactured ("printed") by the Fused Filament Fabrication (FFF) process are usually limited by the cohesion achieved between melt-processed thermoplastic filament strands perpendicular to the filament deposition direction. This significantly limits the usefulness of the FFF process and commercial FFF printers for the production of a wide range of functional components and consumer goods, so that the FFF process is currently used for the production of prototypes for visualization purposes only. In order to open up potential markets for structural components in the future, the realization of an optimized bonding layer quality via a significantly improved cohesion between the filament strands is essential. Since the mechanical properties of polymeric materials generally depend on the density of molecular entanglements and tie molecules in the material structure, it is of the utmost importance to realize the highest possible density of such entanglements and tie molecules between the individual filament layers also in FFF components. The present work deals with different methods of heat input to improve the entanglement and tie molecule density in the bonding layer of FFF components through enhanced polymer diffusion at temperatures far above the glass transition temperature for amorphous plastics or the melting temperature for semi-crystalline plastics, respectively. Heat can be either globally or locally introduced by conduction, convection, and radiation, the latter being the most effective for the FFF process when applied locally via properly controlled laser radiation. Ideally, a compact, cost effective and easy to use radiation source is used for this purpose. Hence, a setup based on a diode laser is presented in this work. Furthermore, an idealized calculation of the amount of heat required to promote the formation of interfilament bonds and thus to achieve an increased mechanical property profile was carried out. Two types of materials commonly used for the FFF process, polylactic acid (PLA) and acrylic-butadiene-styrene copolymer (ABS), were used for the experimental procedure. After producing a special monofilament with improved laser absorption characteristics, test specimens were produced. As a reference, test specimens made of the same materials were printed with the conventional FFF process. The differently manufactured test specimens were characterized optically and visually, using a stereomicroscope, and mechanically, using tensile tests. In addition, specimens were produced with a specially designed device for local heat input onto the substrate layer region just ahead of the new filament deposition. The effectiveness of this laser-assisted method could be proven in tests by adjusting the process parameters of the FFF process. After finding the optimum printing speed (equivalent to the laser power applied) for the materials PLA and ABS, an optical examination of the fracture surfaces of test specimens with filaments laid down perpendicular to an applied tensile load showed a significant increase in plastic deformation capacity, indicative of an improved interfilament bonding. This was confirmed by the mechanical property values determined in tensile tests. Thus, for optimized printing speeds, an increase in tensile strength values of ~20% for PLA and ~7% for ABS was achieved. For elongation at break, the improvements were ~21% for PLA and ~34% for ABS, respectively. The methodology of laser-assisted FFF printing thus offers great potential for mechanically and structurally optimized functional components with specifically introduced anisotropy.

* Corresponding author.
E-mail addresses: gerhard.braeuer@atn.nu (G. Bräuer), klaus.sachsenhofer@jku.at (K. Sachsenhofer), reinhold.lang@jku.at (R.W. Lang).

https://doi.org/10.1016/j.addma.2021.102105
Received 10 August 2020; Received in revised form 14 April 2021; Accepted 8 June 2021
Available online 10 June 2021
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1. Introduction

The Fused Filament Fabrication (FFF) process is the most important material extrusion process in Additive Manufacturing and offers an efficient way of realizing components, some of which are highly complex. However currently, these are limited primarily to the production of visual prototypes, as conventional methods have not been able to achieve sufficient mechanical strength to date. This paper is dedicated to this core topic, specifically to a methodology that improves the bonding and cohesion between the printed layers and thus enables an increase in mechanical properties for more demanding structural applications of FFF parts. In other words, this is expected to enable the leap from the production of visual prototypes to structural components [1-4]. For this purpose, it is necessary to understand and discuss the reasons for the formation of interfilament cohesion and the resulting increase in mechanical strength values on a molecular level. Considering the general recognition of the importance of polymer entanglements and the subsequent formation of entanglements and tie-molecules [8], the movement of the molecular chains and the formation of interfilament entanglements are only sufficiently formed at temperatures far above the glass transition temperature for amorphous plastics or the melting temperature for semi-crystalline plastics [5,8,12-14]. Clearly, there are natural limits to the amount of introduced heat, as unintended material degradation occurring at too high temperatures has to be avoided. A discussion of different heat introduction methods has shown that the contribution of heat conduction is negligible [12,15,16]. Therefore, heat input by convection or radiation has to be considered, whereas this paper refers to the latter, specifically to the heat input by laser radiation.

2. Theory

2.1. Creating interfilament bonding and cohesion

The FFF process produces a layered structure, with the interlayer-strength being determined by the thickness and quality of the "weld seam" between the filament strands, which also represents the weak point of the component [2,17]. The FFF process in particular has become the most widely used generative manufacturing method due to its relatively low extrusion temperatures and wide range of materials available. However, the bond between the filament strands, or rather the resulting "weld seam", shows significantly lower strength values compared to conventional manufacturing processes such as injection molding. This fact can be explained by the insufficient interfilament bonding, since the layer to be extruded is usually deposited onto a layer that has already solidified and cooled down considerably [2,3,5,18,19].

The FFF process is a predominantly thermally controlled methodology, which makes an explicit consideration of the temperature history indispensable. As already stated, the temperature history has a direct effect on the entanglement behavior and the mechanical strength of the final product. As a rule, in the case of amorphous plastics, these entanglements are only sufficiently formed at temperatures far above the glass transition temperature $T_g$, since otherwise the mobility of the chain molecules is too low to form a sufficiently entangled polymer network. Hence, a good degree of interfilament bonding requires thermal melting with a sufficiently high thermal energy in the material for polymer interdiffusion between the layers to occur [20-24].

The supply of heat in the FFF process represents a complex function of the thermal properties of all relevant FFF process and device system parts and is based on the interaction of various parameters. These include the heat output of the print head, the properties of the material used, as well as the filament diameter and volume flow [21,22,25,26]. Immediately after extrusion of the molten filament strand, for amorphous polymers its temperature is far above $T_g$, which initially favors the formation of interfilament bonds. The strand then cools down continuously, which gradually restricts the mobility of the molecules and prevents the formation of interfilament entanglements. This cooling process shows a physically complex, non-linear behavior, which requires a modelling of the heat transfer in the FFF process to provide an estimation of the temperature profile during the cooling process [22]. As a relatively simple but sufficient model for this application area, the method of lumped capacity can be used [13,27].

For using the lumped capacity method, in the present work the following assumption were made:

1. uniform temperature distribution over the entire strand cross-section
2. semi-infinite strand length
3. constant heat transport and heat convection coefficients

Based on these assumptions it is possible to reduce the cooling process of the filament strand to a one-dimensional, non-linear heat transport model. Fig. 1 shows a simplified model of the FFF process. A filament strand of elliptical shape is extruded at the printing speed $v$ in the direction of the X-axis, with the reference coordinate in the print head. Due to the much higher mass of the printing bed compared to the extruded filament, successive heating of the bed is neglected. For the mathematical derivations and solutions of the differential equations, reference is made here to the literature, with the presentation of the graphical solution being a more illustrative alternative [13,27].

The cooling curves of the filament strands of an ABS type are shown below (Fig. 2). This is a comparison of the temperature-time curves according to two different methods, namely the simple so called lumped capacity method and the more complex model according to Rodríguez [28], which is based on Finite Element (FE) calculations. The latter provides more precise results and shows in particular that a substantial part of the cooling takes place within a very short time (less than one second) immediately after the filament deposition. Furthermore, various experiments with this type of ABS have shown that no pronounced formation of interfilament bonds occurs at deposition temperatures below ~200 °C. Taking into account that the $T_g$ value for this material is 94 °C, these results show that at the filament surface deposition temperature, the $T_g$ values must even be about 100 °C above the $T_v$ values in order to generate sufficient interfilament cohesion. Furthermore, it follows from Fig. 2 that at an extrusion temperature of 270 °C the deposition temperature (defined as the average temperature of the laid down filament according to filament centerline and top of filament in Fig. 2) is already undercut after about 0.5 s. In other words, these experiments show that the time window for the formation of sufficient interfilament bonding is much shorter than the cooling time of the filament strands to the glass transition temperature of 94 °C, which is the case after about 5.6 s [13,20].

According to Rodríguez, the formation of interfilament bonds between two filament strands in the FFF process can be described in three steps as shown schematically in Fig. 3 for ideally circular filament cross
sections. The first step in this process corresponds to pure surface contact by wetting when the strands first come into contact. Immediately afterwards, the strands deform in the interfilament zone due to the molten state of the filaments when lightly pressed. The actual interdiffusion of molecular chains then takes place in the third step [13,27,29]. For a good binding quality, in addition to the temperature requirement of more than 200 °C, a large ratio of the weld line radius (2y) to filament radius (2a) should be aimed for. The development of strength in FFF manufactured objects therefore requires a controlled thermal process in which any introduction of additional thermal energy promotes the formation of interfilament bonds, whereby different options for heat input must be evaluated for their effectiveness in this process.

2.2. Methods of heat input

Currently conventional FFF systems use a heated printing platform and ideally a closed, heated printing chamber. Since the temperatures that can be set with these systems remain below the temperature ranges relevant for sufficient interfilament bonding, the strength increases that can be achieved by varying the temperature parameters are also very limited [25,30]. Temperature adjustments in conventional FFF processes are therefore often made with the aim of minimizing unwanted side effects such as warpage and shrinkage. Furthermore, a closed, heated chamber is also limited by the heat deflection temperature (HDT) of the material being processed, i.e. at temperatures far below the temperatures required for effective interfilament bonds, since global exceeding of the HDT temperatures leads to instabilities of the entire part during manufacturing. Therefore, alternative methods have to be found to introduce heat into the material in a more efficient and targeted way.

The three basic physical principles of heat transfer are heat conduction, convection and heat radiation. In the case of heat conduction, the heated printing bed should be considered. However, an increase of the printing bed temperature can lead to various problems, e.g. concerning component instability and uneven heat distribution in the part. In addition, heat conduction via the printing bed allows only a planar input, but no local input of heat, which is essential for the formation of interfilament bonds [25,30,31].

For heat input by convection, the closed, heated printing chamber results in similar problems as for heat conduction via the heated printing bed. Here too, heat transfer occurs globally over the entire surface of the part. Although a more targeted local heat input in the immediate printing area is possible when using hot air nozzles (Fig. 4), the exhaust air jet prevents a heat input that is only concentrated on the immediate filament deposition zone, so that larger surrounding regions are also heated by the hot air stream. This can ultimately lead to part instability [32].

In contrast to the options mentioned above, heat input by means of thermal radiation allows a simple way of supplying heat locally in the interfilament “weld line” area. There are two possibilities of heat input by radiation, one of which is already widely used in the field of plastics technology. This applies to heat input by infrared radiation, which is used for the production of large-volume components using the material extrusion process (Fig. 5) [33]. Alternatively, heat can be supplied very locally using a laser as a radiation source (Fig. 6) [12,16]. In contrast to infrared radiation by means of infrared lamps or a heated mass e.g. in the form of a metal block [34], an even more targeted heat input is possible by focusing the laser on the specifically desired area. If the laser is also focused on the filament strand that has already been deposited and cooled down immediately before the new extruded filament is laid down, two melting zones meet directly, which is particularly advantageous for the formation of a high density of interfilament bonds by molecular entanglements.

2.3. Interaction of radiation and polymers

The principles of interaction between radiation and matter are important for understanding the laser-assisted methodology used in this work. Since the absorption behavior is largely controlled by the material used and its properties, it is essential to take a closer look at the basic interactions between material and radiation. The four basic parameters of radiation polymer interactions to be considered are reflection, absorption, transmission and refraction (scattering). When radiation passes from one medium to another, with different refractive indices, it is scattered if the interface between the materials has irregularities greater than the wavelength of the incident radiation. This relationship...
is particularly noticeable in semi-crystalline polymers, as the amorphous and crystalline structures, and the interaction of the radiation with these areas, make them appear opaque by refraction. For this reason, amorphous polymers are also transparent, in contrast to the semi-crystalline ones. When light is incident on matter, a certain part of the radiation is reflected, while the rest penetrates the material, is absorbed, scattered or transmitted [35]. In their basic composition, polymers generally show little or no absorption in the wavelength range of visible light and the near infrared range (Fig. 7). Chemically, this is due to the fact that the majority of polymers consist of single bonds, isolated double bonds and benzene rings. Such molecular structures show a strong absorption of electromagnetic radiation in the infrared and ultraviolet range.

2.4. Heat input by laser radiation

Due to the above-mentioned discrepancy in the radiation absorption spectrum of plastics, the question now arises, which type of laser radiation is a relevant option. The range of lasers used in industrial applications extends from CO$_2$ lasers to neodymium lasers and diode lasers.

2.4.1. CO$_2$ laser

The CO$_2$ laser is one of the most frequently used lasers for industrial applications, especially for material processing with an efficiency of up to 20% and laser powers up to 100 kW in continuous operation. By excitation of the CO$_2$ molecule to different vibration conditions, light is emitted in a wavelength range of 10.6 $\mu$m. This excitation can take place by means of electron impact or even more frequently by an excited N$_2$ molecule [37,38].

2.4.2. Neodymium-doped yttrium aluminum garnet laser (Nd:YAG laser)

The neodymium laser belongs to the solid-state lasers, which have a crystalline substance as an embedding medium for the neodymium ion. As host material or laser host, there is a variety of possible components, but for industrial laser systems, yttrium-aluminum-garnet has become the preferred material because of its high gain and good mechanical and thermal properties. The laser is excited by absorption of radiation from the crystal. The wavelength of 1064 nm results from the emission of light through the transition from the upper to the lower laser level of the neodymium ion. The shorter wavelength compared to the CO$_2$ laser offers the advantage that optics made of standard glass can be used and that the laser beam can be transported through fiber-optical devices. A main field of application for this type of laser is in science and technology development, especially in applications in medicine, spectroscopy, material processing and metrology [37,38].

2.4.3. Diode laser

Semiconductor lasers or diode lasers differ from other lasers in the way they are excited. This is done by supplying current in contrast to the optical pumping of solid-state lasers. This effect results from the special properties of indirect semiconductors (such as gallium arsenide or indium phosphide) in combination with different doping (p-doping & n-doping). The direct excitation results in high efficiencies of more than 50%. Despite the high power density, only absolute power in the watt range can be achieved for technical and physical reasons. An increase in power (up to approx. 60 W) can be achieved by interconnecting several diode lasers to form diode laser arrays or bars. Diode lasers are typically in a wavelength range of 790–1080 nm, which leads to applications in telecommunications, material processing and medical technology [37,38].

These various types of lasers differ mainly in the wavelength of their emitted radiation. CO$_2$ lasers are frequently used in the field of plastic welding, as they are the only sources of radiation in a wavelength range in which the plastic absorbs energy. However, CO$_2$ lasers are not very well suited for the application in FFF due to the size of the laser, the cost of the laser and the need for additional fiber-optics to focus the beam. This increases the overall complexity of the System and can be an obstacle especially in low-cost printer settings. For this reason, a compact, cost effective and easy to use diode laser is an attractive alternative in this regard. However, when using such a type of laser (diode laser as well as Nd:YAG laser) whose wavelength range is in the non-absorptive spectrum of plastics (UV to near infrared range), it is necessary to incorporate a suitable additive into the plastic by compounding so that it becomes absorptive in the desired radiation range of the laser.
3. Experimental

The theoretical part of this chapter is dedicated to a pragmatic consideration of the heat input, based on the basic relationships described above and their significance for further optimized interfilament bond strength, in order to quantify the relevant physical parameters. Hence, only the introduction of energy in the form of heat radiation by laser is explicitly considered here, as this method is best suited for the targeted, local supply of heat. The case under consideration is that the laser is locally focused on the already deposited filament strand (substrate) before the molten filament strand to be newly deposited is applied. The practical part deals with the selection of the material, the filament production, and the production of the test specimens using the new FFF methodology. Furthermore, below the selection of test specimens as well as the measuring devices used are discussed.

3.1. Simplified idealized calculation of the required amount of heat

Using simple thermodynamic considerations the required laser power can be determined as follows [15,39]. This makes it possible to calculate the heat flow \( \dot{Q} \) as the heat power required to heat the plastic to a certain temperature as a function of the printing speed \( v_p \).

The specific heat capacity \( c_p \) of a substance is defined as follows:

\[
c_p = \frac{\Delta Q}{m \cdot \Delta T} \tag{1}
\]

\( \Delta Q \) heat supplied or dissipated [J]

\( \Delta T \) temperature difference [K]

\( m \) mass [kg]

This results in the required heat output as heat flow for increasing a given mass flow by a defined temperature level as follows:

\[
\dot{Q} = \dot{m} \cdot c_p \cdot \Delta T \tag{2}
\]

\( \dot{Q} \) heat flow [W]

\( \dot{m} \) mass flow [kg/s]

For the FFF method, the mass flow \( \dot{m} \) is calculated as a function of the printing speed \( v_p \) according to:

\[
\dot{m} = \rho \cdot v_p \cdot A \tag{3}
\]

\( \rho \) material density [kg/m\(^3\)]

\( v_p \) printing speed [m/s]

\( A \) area to be melted [m\(^2\)]

The depth cross-sectional area \( A \) of the already deposited filament strand to be melted by the laser results from the product of extrusion width and desired sub surface melting depth as follows:

\[
A = W \cdot D \tag{4}
\]

\( W \) extrusion width [mm]

\( D \) subsurface melting depth [mm]

For the heat output as heat flow it follows:

\[
\dot{Q} = \rho \cdot v_p \cdot W \cdot D \cdot c_p \cdot \Delta T \tag{5}
\]

Assuming a local temperature increase of the substrate strand to the temperature of the extrusion strand follows for \( \Delta T \):

\[
\Delta T = T_{\text{extrusion}} - T_{\text{substrate}} \tag{6}
\]

\( T_{\text{extrusion}} \) extrusion temperature [°C]

\( T_{\text{substrate}} \) substrate temperature [°C]

For the quantitative determination of the required maximum heat flow \( \dot{Q} \) under the above simplified and idealized assumptions, corresponding parameters for the printing and material parameters for polylactic acid (PLA) and acrylonitrile-butadiene-styrene copolymer (ABS) are listed in Table 1. For the temperature difference \( \Delta T \), a worst case scenario was assumed in which the substrate has already cooled down completely to room temperature (20 °C). The assumed temperature difference hence depends on the extrusion temperature which was 210 °C for PLA and 260 °C for ABS (see Table 3).

| Table 1 Printing and material parameters for calculating the required heat flow for PLA and ABS. |
|---------------------------------------------------------------|
| Material | PLA | ABS |
| Printing speed \( v_p \) [mm/s] | 0–100 | |
| Extrusion width \( W \) [mm] | 0.60 | |
| Melting depth \( D \) [mm] | 0.05 | |
| Density \( \rho \) [kg/m\(^3\)] \(^a\) | 1240 | 1050 |
| Specific heat capacity \( c_p \) [J/kg*K] \(^b\) | 2137 | 1300 |
| Temperature difference \( \Delta T \) [°C] | 190 | 240 |

\(^a\) from data sheet [40,41] \n\(^b\) from literature [42,43]
The heat flow calculated as a function of the printing speed according to equation 3.5 is shown in Fig. 8 for the two materials PLA and ABS. It should again be noted that these results are based on ideal assumptions and therefore do not provide an exact representation of reality. A determination of the needed laser power based on these results requires knowledge of all relevant losses. These include the efficiency of the radiation source, the radiation losses to the environment and in the material. Corresponding efficiencies of the diode laser are listed as range for PLA and ABS in Table 2. From the literature [12,16,37,38] and our own measurements [44], overall efficiencies of \( \sim 20-65\% \) result, depending on the radiation source used. In other words, the laser power should be up to 5 times higher than the heat flow shown in Fig. 8.

3.2. Material selection and filament production

The focus of the material selection for this work was on common materials for the FFF process, in this case polyactic acid (PLA) and acryl-butadiene-styrene copolymer (ABS). These materials are well suited for this process. PLA has a low degree of crystallinity and ABS is an amorphous polymer. Hence in both cases low shrinkage and warpage can be expected. In addition, it should be noted that PLA is extremely brittle while ABS is rather ductile, so that the choice of material covers both types of material behavior. Since the filament was produced in-house, the extrusion types PLA ‘Ingeo 3D850’ (NatureWorks LLC, Minnesota, USA) and ABS ‘Magnum 3404’ (Trinseo, Pennsylvania, USA) were selected.

For the methodology applied in this work a diode laser with 808 nm wavelength was used. To enable absorption in the range of the wavelength of the diode laser, it was necessary to incorporate a suitable additive into the two materials. The absorptive additives designated Lumogen (Treffert GmbH & Co. KG, Bingen, Germany) were added in the course of filament production in the form of master batches in the compounding process for the materials PLA and ABS. As an example, Fig. 9 shows the effects of two Lumogen additive types on the absorbance spectrum of a polycarbonate sheet. It can be seen that there is a significant increase in the absorbance in the desired range of 808 nm and a related increase in the absorption of energy by radiation. The specific additive used in the materials for this investigation cannot be published for secrecy reasons.

In order to enable sufficient interfilament bonding, the majority of the laser radiation should be absorbed to a depth of about 100 µm. For this purpose, the required amount of additive was calculated using the Lambert-Beer law [45]. For both materials, PLA and ABS, plates of different thicknesses but equal master batch concentrations of 5 wt% were produced. The extinction was measured by UV-Vis spectroscopy at a wavelength of 808 nm, i.e. the wavelength of the diode laser. A linear regression of these data points allowed to determine the extinction coefficient from the slope of these fit functions. Using this extinction coefficient, curves corresponding to higher master batch concentrations up to 20 wt% were constructed.

Fig. 10 shows these curves for the materials PLA and ABS. For a better understanding of the extinction spectrum, the extinction is shown as percentage absorption of the radiation by means of the grey, dashed lines parallel to the x-axis. Since 100% radiation absorption at the assigned absorption depth of about 100 µm leads to disproportionately high master batch concentrations, a compromise of 14 wt% (corresponding to 80% absorption) was chosen for the material PLA and 16 wt% (corresponding to 70% absorption) for the material ABS. The reference measurements correlated with the theoretically calculated curves to sufficient accuracy (see reference measure points Fig. 10). After determining the required quasi-optimized master batch concentrations for both materials, the filament could be produced on the institute’s own filament compounding/extrusion line (Fig. 11).

3.3. Specimen selection and manufacture

In order to shorten the production time of a large number of specimens for the required tests, alternative specimen shapes were selected and used on the base of previous testing experience [44]. Although the 5A test specimen according to ISO 527-2 [46] offered a time and material saving option at first, it proved to be unsuitable for determining the mechanical properties in 90° orientation due to its narrow cross-section. Therefore, a thinner and more compact version of the 1A test specimen according to ISO 527-2, here designated as “mini test specimen” was chosen, which could be measured with the same test conditions due to its geometric similarity. A comparison of the test specimen configurations with geometrical data is shown in Fig. 12.

After determining the preferred test specimen geometry, the Simplify3D software was used to generate the G-code for the printing in 90° orientation. The system used was a DIY printer of type P802QR2.
(Zonestar Innovation Technology Co., Shenzhen/CN) with an installation space of 220 × 220 × 240 mm
3, a maximum processing temperature of 275 ◦C, a maximum printing speed of 150 mm/s, and a heated
print bed. The setup was based on the Cartesian coordinate system. A schematic drawing of the FFF system is depicted in Fig. 13 (a). The printing parameters used are shown in Table 3.

The laser used is a diode laser with 4 W nominal power, which radiates at a wavelength of 808 nm, i.e. in the near infrared range. It was mounted on a carrier plate on the back of the print head by means of a joint rod (see Fig. 13 (b)). Hence, there is no need for additional beam guiding systems such as mirror based solutions [16] or fiber optics [12]. Furthermore, Fig. 13 (c) shows that the focus of the laser is positioned directly in front of the printing nozzle to introduce energy at the same time into both, the previously deposited substrate layer and the instantaneously printed filament strand.

3.4. Measuring instruments and measuring conditions

To generate the extinction curves shown in Fig. 10 above, a UV-Vis/NIR spectrophotometer of the type Lambda 950 (Perkin Elmer, Massachusetts, USA) was used. The test plates were examined with regard to their optical characteristics in a wavelength range from 250 nm to 2500 nm.

A qualitative assessment of interfilament bonding was done by visual/optical analysis. Fracture surface images of the tensile test specimens were recorded with the stereomicroscope type SZX16 (Olympus, Hamburg, Germany).

Mechanical tests were conducted with a universal tensile testing machine 2020 (ZwickRoell, Ulm, Germany). The modulus of elasticity, the yield and/or fracture strength (defined as tensile strength) and the elongation at break were evaluated. The testing rate for the determination of the modulus was 1 mm/min according to ISO 527. After determination of the modulus, the tests were continued with a rate of 5 mm/min until rupture. Mechanical test results were generated using up to seven individual specimens, with mean values and standard deviations reported below.

4. Results and discussion

The diagrams in Fig. 14 show a comparison of the mechanical properties (modulus, tensile strength and elongation at break) obtained for the different specimen configurations of the two printed materials PLA and ABS when produced without laser support. Also shown are the data for the two cases of orientation (0◦-orientation and 90◦-orientation of the filament strands) as upper and lower bound results of the FFF specimens, respectively. For comparison, injection molded 1A test specimens (IM) were produced and are depicted in the diagrams. Such IM specimens were also produced and tested with PLA and ABS material compounds containing 5 wt% of the absorptive additive master batch. The results of these IM specimens reveal that adding the absorptive additive to the materials does not have any significant effect on the mechanical properties. Higher additive loadings for injection molded specimens where not investigated due to limited additive availability. A detailed comparison of all FFF specimen configurations (1A, 5A and “mini test specimen”) and filament deposition orientation (0◦ and 90◦) was performed only for PLA. Based on these results and keeping the primary goal of this investigation in mind (i.e. evaluation of interfilament bonding improvements of laser assisted specimen production), the test program for ABS was reduced to 5A specimens (0◦ and 90◦) and mini
test specimens (90° only).

Looking at PLA as a printing material, the printed 1A test specimens showed increased stiffness over the smaller test specimen shapes (5A and mini test specimens), but lower tensile strength and elongation at break. Except for the elongation at break, where mini test specimens reveal higher values than 5A specimens, the results of these two specimen configurations are in good agreement. This supports the decision to perform laser assisted testing with the mini test specimens only, for which the increased width is believed to represent a more sensitive measure to evaluate the quality of interfilament bonding in 90° specimens.

For assessing the effect and potential of laser assisted FFF printing, several specimen series of 90° filament deposition orientation were produced for different printing speeds without and with the support for applying heat via a diode laser. For this test series, the PLA and the ABS formulations contained 14 wt% and 16 wt%, respectively, of the absorptive additive master batch. Since the available FFF test setup did not allow for a precise intensity control of the laser, the heat input (energy input) was speed-controlled. In other words, as the laser operates at the nominal power level (4 W), the energy input results from the irradiation time of the laser source, which is determined by the printing speed, which was ranging from 5 to 60 mm/s for PLA and from 5 to 80 mm/s for ABS.

These settings of laser power and printing speeds are in good agreement with the choice of parameters in the work of other groups investigating laser-assisted FFF printing. In the setup used by Han et al. [12] a CO2 laser was operated at a power of 0.33–2 W and the printing speed was set to 10 mm/s. Ravi et al. [16] used a diode laser with custom optics system which was operated at a power of 0.75 W in a printing speed range between 1 and 10 mm/s. Considering typical absorbance values of 0.94 [12] and 0.8 [16] these combinations of laser power and printing speed resulted in a comparable heat input as with a laser power of 4 W, a printing speed between 5 and 80 mm/s and an absorbance between 0.7 and 0.8 used in the present study.

The effect of printing speed is illustrated in the bar charts of Fig. 15, comparing results obtained from specimens produced without laser support (blue bars) and with laser support (red bars). The bar charts depict only the ultimate values for tensile strength and elongation at break as these are most sensitive to interfilament bonding quality. For comparison also shown are results for injection molded specimens of neat PLA and ABS not containing the additive (grey bars at the left in each graphic).

In order to identify a trend or influence of the laser support from these results, normalized results are illustrated in Fig. 16. For this data normalization, the values for FFF specimens printed with laser support are divided by the corresponding values of FFF specimens printed without laser support for a given printing speed, all other processing conditions being equal. In other words, a value of 1 for this ratio implies no effect of the laser support in printing the specimens, a value >1 implies a positive effect of the laser application and a value of <1 implies a negative effect of the laser application. The former case (normalized value >1) may be interpreted as an indicator for enhanced interfilament entanglement formation, whereas the latter case (normalized value <1) indicates the onset of a reduced “effective” interfilament entanglement formation due to excessive heating leading to thermo-oxidative degradation in the interfilament region [44].

Overall elongation at break seems to be a more sensitive indicator for the quality of interfilament bonding than tensile strength. For PLA (14 wt%) the normalized value for the elongation at break is about 1 at a printing speed of 10 mm/s. Printing speeds below 10 mm/s lead to a decrease of the normalized elongation at break due to local thermo-oxidative degradation of the material as evidenced by visible fume formation during printing. Printing speeds above 10 mm/s reveal enhanced mechanical performance, showing the highest value for a printing speed of 20 mm/s (improvement of about 20%). Conversely, using again the normalized value elongation at break as indicator, for ABS (16 wt%) the threshold for a positive effect of laser assisted specimen production seems to be at a printing speed of about 15 mm/s, revealing a maximum for the normalized elongation at break at 20 mm/s (improvement of about 35%). At higher printing speeds both materials show some reductions in the normalized mechanical data, and it is to be expected that at even higher printing speeds beyond those investigated the normalized values may again approach 1, since the laser constantly provides less energy input. These findings are in good agreement with data reported in the literature [12,16] were an optimum of strength was found at a specific combination of laser power and printing speeds.

Macroscopic images of the fracture surfaces obtained from tensile specimens (mini test specimen) with 90° filament deposition orientation exemplifying the effect of laser assisted FFF specimen production vs. non-laser assisted specimen production are depicted in Fig. 17. For both material formulations, the printing speed was above the threshold value at which the normalized value for elongation at break is >1 (i.e. 10 mm/s for PLA (14 wt%), 15 mm/s for ABS (16 wt%)), hence,
improved interfilament cohesion by interfilament entanglements is to be expected for specimens printed with laser support. While this is not so clearly visible for PLA (14 wt%) (Fig. 17 (a)), it is quite obvious for ABS (16 wt%) (Fig. 17 (b)). Upon a closer examination of the fracture surfaces another feature is observed. That is, improved cohesion is visible only at every second interface of the filament layers. Indeed, this fact that only every second layer is melted is a result of the experimental setup. Thus, the one-sided use of the laser source (Fig. 13 (c)) relative to the two-directional back-and-forth movement of the heated printhead ensures that the already deposited substrate layer ahead of the printhead is heated by the laser only when moving in the direction where the laser is focused. On the way back, the laser focus happens to be in the wake of the filament deposition. This drawback could be resolved in future FFF equipment designs incorporating circumferential laser arrays positioned around the nozzle or by a single laser equipped with an adequate laser beam guiding system.

5. Summary and conclusions

The method of heat input by laser radiation used in this work proved to be a valid approach to create improved interfilament bonds and a corresponding increase in the mechanical property profile. An important prerequisite is, however, to adjust the laser radiation source to the radiation absorbance of the polymer or vice versa. For diode laser sources, as the one used in the present investigation, this implies to include an adequate amount of a radiation wavelength specific absorbance additive in the polymer compound.

From a methodological-scientific perspective with regard to a systematic and efficient test program, the choice of the mini test specimen led to a significant reduction of the required printing time and thus to an increased efficiency in carrying out this research work. The comparison of the mechanical properties of the different test specimen configurations and geometries confirmed the choice of the mini test specimen for investigating the potential of a laser assisted FFF printing process. For optimized processing conditions improvements in elongation at break

![Fig. 14. Comparison of the mechanical properties (modulus, tensile strength and elongation at break) of the two printed materials PLA (a-c) and ABS (d-f) for different specimen geometries.](image-url)
perpendicular to the filament deposition orientation of up to 20% and 35% could be achieved for PLA and ABS, respectively, when modified with an radiation absorbance additive. And yet, while the mechanical properties of FFF manufactured test specimens come quite close to injection molded specimens of the same material when tested in filament deposition direction, the values achieved perpendicular to the filament deposition direction still remain significantly below those obtained for injection molded specimens. This emphasizes again that great attention must be paid in FFF produced components on the optimization of the filament orientation deposition when structural applications of components are envisioned. And yet, there is still some potential for further improvements in laser assisted FFF processes to reduce and minimize the drawback in mechanical performance due to a limited interfilament bonding.

Fig. 15. Mechanical properties of the test series without and with laser application as a function of the printing speed for PLA (a-b) and ABS (c-d). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 16. Normalized values for tensile strength and elongation at break as a function of printing speed for PLA (14 wt%) (a) and ABS (16 wt%) (b).
The authors declare the following roles: Gerhard Bräuer: Conceptualization, Resources, Investigation, Data curation, Methodology, Visualization, Formal analysis, Writing – original draft, Writing – review & editing. Klaus Sachsenhofer: Investigation, Data curation. Reinhold W. Lang: Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

The effort by Markus Gall (Johannes Kepler University, Linz - Institute of Polymeric Materials and Testing) in proofreading the manuscript is gratefully acknowledged.

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

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