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Development of a characterization approach for the sintering behavior of new thermoplastics for selective laser sintering

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Invited Paper

Abstract

Currently the standard thermoplastic powders for selective laser sintering are based on polyamide12. This leads to restrictions for many applications e.g. in the industrial or medical field. Thus, research on further polymers with enhanced chemical or higher thermal stability plays a major role for applying additive manufacturing to serial production of individual components. Currently, great efforts are made to process new technical thermoplastics like polypropylene or polyetherketones by selective laser sintering. In this paper, the suitability and processing behavior by means of melting and (isothermal) crystallization are studied, and a method for the qualification of new materials is presented. Based on this method processing parameters for new thermoplastics can systematically be found.

Keywords: Selective Laser Sintering; Additive Manufacturing; Isothermal Crystallization; POM; PP; PA2200; PE; PEEK HP-3

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1. Introduction

Formerly, techniques of additive manufacturing were used to serve merely for prototype construction of special products. This has clearly changed, as they are now used for a vast number of new fields of application by means of direct manufacturing. Especially for technical parts, products made by additive manufacturing have grown in importance, now being much more than mere objects for demonstration [2]. In particular, powder-based plastics processing techniques, such as selective laser sintering (SLS) and selective mask sintering (SMS) generate good component properties and thus gain more interest [3]. In contrast to this benefit, the range of materials suitable for processing by this technique is very much restricted to polyamide12 (PA12, e.g. PA2200, EOS GmbH), polyamide11 (PA11, e.g. Primepart DC, EOS GmbH), polystyrene (PS, e.g. Primecast, EOS GmbH), and, in very few cases, thermoplastic elastomers (TPE) [4-5]. Currently, there is a growing number and variety of applications which require components that can withstand high mechanical load, have a high density and a variety of other possible characteristics like biocompatibility. A material such as PA12 is therefore no longer sufficient to meet the high demands posed to components suited for serial production. This is why there are new semi-crystalline thermoplastics, e.g. polypropylene (PP) or polyetherketone (e.g. PEEK-HP3, EOS GmbH) on the verge of entering the market.

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2. Motivation

The investigations presented in this paper are focused on improving current laser sintering technology by means of adding new materials and giving an understanding of occurring processes as basis for direct manufacturing in the future. Regarding options of usage for other types of thermoplastics, technologies such as SLS may be more competitive too, if part properties are different from those of PA12 in combination with the good process ability. It is therefore essential that significant mechanisms of interactions (e.g. in the molten part) are understood and a subsequent material and process specific characterization is done, in order to adequately process the material. Much of the knowledge available on the process at present is based only on the processing of PA12 as a semi-crystalline thermoplastic [6] and amorphous materials like polycarbonate (PC) [7-8]. Especially, melting and solidification behaviours must be known because they are of outstanding importance for the laser sintering process. Thermo analytical methods of analysis for various semi-crystalline thermoplastics are suitable to show which major material properties have an effect on the process ability by SLS. Based on the established model of a quasi-isotherm laser sintering process [9] the influence of time-dependent crystallization effects is studied to enhance the existing model. In this study, polyamide12 (PA12), polyoxymethylene (POM), high density polyethylene (PE-HD), polypropylene (PP) and polyetherketone (PEEK HP-3, EOS GmbH) are submitted for testing with regard to their processing behaviours, and resulting component properties.

3. SLS Process and Resulting Demands on Thermoplastics

During manufacturing, the plastic powder is applied, layer by layer. The powder that is located at the interface with the component is fused selectively by a CO_2 laser, and thus connected insolvably to the melt layer below. The surrounding powder, that was not molten, supports the generated melt. Current models assume that the processed part fully remains at a molten state until all layers of the component have been produced. Then the powder bed, with its components inside, is cooled down as a whole [9]. This processing technique demands that the material fulfils a series of requirements.

3.1. Requirements to Plastic Powder

The properties of laser sintered parts, e.g. density, surface topography, accuracy of detail and dimension are determined by process parameters interacting with the material. In investigations, it was revealed, for instance, that the geometry of particles is a decisive factor that substantially determines component coarseness [9-10]. The size distribution and geometry of particles are of major importance for sintered parts' porosity. On the one hand, high powder density leads to higher part density, dimensional accuracy and strength in the sintered parts, yet it may deteriorate flowabilities on the other hand. Commercially available laser sintering powders with good flowabilities consist in general of spherulite particles with a narrow size distribution of $d = 60$ µm, and with a low share of fine particles below $d = 10$ µm [11].

Considering the long building times, the polymer must particularly resist thermal degradation, since it is kept at a temperature close to the crystalline melting point for several hours. At the end of the production process, the thermally degraded powder, that was not molten, is separated from the laser sintered component and will be recycled, if possible. In an ideal case, the powder should not be agglomerated, so that the part can be separated from the remaining powder merely by making use of the force of gravity. Due to ageing during building, the powder's material properties change, which is why the remaining material must be mixed with up to 50 wt.-% of virgin powder [12].

3.2. Thermal Boundary Conditions

Apart from material application, temperature control during building is of major significance for the part's profile of properties. For part density, a closed melt film is crucial, making it necessary for the powder material to have low melt viscosity. Due to their wide range of softening and the resulting possibility of achieving low component densities, as well as a high dimensional stability, amorphous thermoplastics are employed e.g. as lost cores in precision casting [11]. Thus, for direct part manufacturing, only semi-crystalline polymers are relevant at present.

Semi-crystalline plastics, however, are heated to the point above glass transition temperature, close to the crystalline melting point, with the laser merely fusing the crystalline shares. Due to the high chain mobility, decrease in viscosity is much steeper after exceeding this narrow range of crystalline melting, Fig. 1 (right) [13-14].

In an ideal case, the building process would lead to the model state of quasi-isotherm laser sintering, where melt and solid powder exist side by side. The building process is carried out in a sort of two-phase mixing state. The laser merely introduces the energy that is necessary for the material to exceed the point of phase transition. For the subsequent creation of a coalesce film and thus fully dense parts the melting viscosity and surface tension are just as significant as the before shown powder density and flowability of laser sintering powders [15-16]. Temperature increase in the surrounding powder bed should be as small as possible, here. Another requirement of this process, in terms of material properties is that: The plastic material's crystallization temperature should be clearly below the crystalline melting point, Fig. 1 (left). In case the initial melting temperature is exceeded, powders will start to melt, whereas, if temperature is below initial crystallization temperature, the plastic melt produced up to then will start to crystallize, causing shrinkage respectively curling. Dynamic Differential Scanning Calorimetry (DSC), among others, can describe phase transitions, and thus the differences in temperatures between crystalline melting and crystallization. On this basis, the possible range of processing temperatures during SLS production may be defined. Here it is desirable that the temperature between melting and crystallization along with the melting peak are high with a narrow temperature range for the melting process itself.

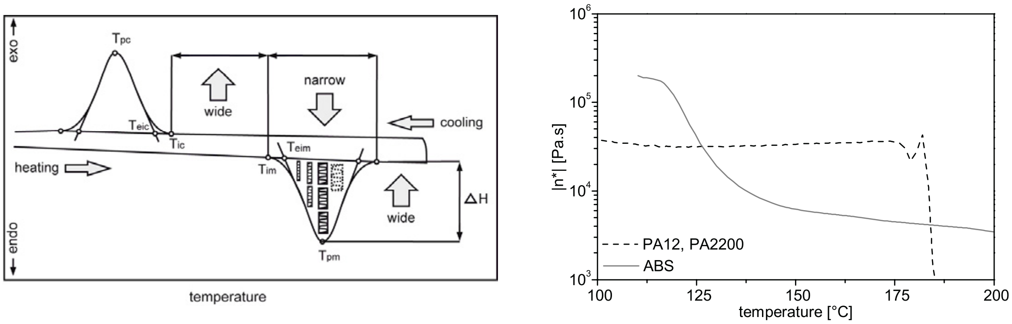


Fig. 1. left: theory of quasi-isotherm laser sintering process (schematic)
right: viscosity loss of ABS (amorphous) and PA12, PA220 (semi-crystalline)

4. Materials and Methods

4.1. Materials and Powder Preparation

Commercially available laser sintering powders made from PA12 (PA2200, EOS GmbH) and PEK (PEEK HP-3, EOS GmbH) were tested as to their processing properties and compared to POM, PE-HD and PP powders.

Table 1. Properties of investigated polymers (from molded specimen) [1]

	E-modulus [N/mm²]	σ_{yield} [N/mm²]	ε_{break} [%]	T_{melt} [°C]
PA12	1400	50	~ 200	170 - 180
PP	1400-1800	25 - 40	> 50	160 - 165
PE-HD	600 - 1400	18 - 30	> 50	125 - 135
POM	2600-3200	60 - 75	20- >50	175
PEEK	3700	100	> 50	335

In Table 1 an overview of the characteristics for the investigated materials is shown to give an overview of attainable part properties [1]. Generating spherulite particles directly from polymerization is not possible with all types of plastics. As an alternative, powders can be converted from pellets. Cryoscopic grinding is a well-proven method to make powder particles with a size less than 100 µm, as necessary for laser sintering. The pellets are cooled down to T_{mill} = -50°C in a cooling section and fed into a counter-rotating pinned disc mill (impact crusher principle). After milling, the powder is classified and screened down to a desired particle diameter. Cryoscopic grinding to a particle size below d = 80 µm was done with POM.
POM powder was mixed with 0.2 wt.-% of Aerosil®, in order to step up flowability. In IR measurements conducted on PE-HD before, the material was found to have a high transmission coefficient when submitted to the wavelength of the used CO_2 laser (λ = 10.6 µm). By adding 0.4 wt.-% of Carbon Black® the penetration depth of the laser could be limited to approximately 100 µm. As a result, the parts were black, had a high degree of absorption and better flowability.

4.2. Thermoanalytical Investigations

To investigate the melting and crystallization behavior of the thermoplastic material employed, the SLS process was simulated by DSC measurements. According to DIN 53765, 10 or 20 K/min is the standard heating and cooling rate, for thermoplastics. However laser sintering is a slow process of part generation, which makes standard measurement technologies unsuited to sufficiently describe the real process. The temperature is kept close to the crystalline melting point (T_{pm}) for a long period of time, and new preheated layers are applied on top of the previously sintered ones. For this process, a model is available [5, 9]. As a result of tests performed this model was supplemented by the time-related process of crystallization. Therefore, several heating and cooling rates (10/5/1 K/min) were carried out with samples of about 5 mg and resulting heat flows were measured.

The idea of quasi-isotherm laser sintering implements the assumption of melt which does not crystallize for a long period of time at a point just below its melting point. With crystallization related to time and temperature, further DSC tests were carried out alongside the laser sintering process. The specimens were heated in a defined program to T = T_{pm}+20 K at 20 K/min, cooled down to measurement temperature at a cooling rate of 40 K/min and kept in the isothermal state at different temperatures above the determined beginning of crystallization,
Fig. 2. The exothermal heat flows and crystallization times (the time between the beginning of the isothermal measurement t_0 and crystallization peak t_{pc}) were recorded. In a preprocessing the PA12 material was submitted to previous drying (in N_2) at 120 °C for 15 minutes in the DSC, since otherwise the results were not reproducible due to degradation and cross-linking. With the resulting DSC-curves crystallization times could be analyzed at different temperatures and a model for crystallization kinetics could be derived due to following differential equation:

$$\frac{d\alpha}{dt} = f(\alpha)k(T) \tag{1}$$

with:
$d\alpha/dt$ = reaction/crystallization rate (min^{-1})
α = crystallization conversion
k(T) = specific rate constant at temperature T (min^{-1})
$f(\alpha)$ = conversion function

When considering a quasi-isotherm process the common Šesták-Berggren kinetic model is suitable [17]:

$$f(\alpha) = \alpha^{m}(1-\alpha)^{n} \tag{2}$$

where *n* and *m* are partial reaction order terms. In order to describe the change of crystallization rate as a function of temperature the Arrhenius equation can be used for homogeneous kinetics [18]:

$$k(T) = Z \cdot e^{-E_A/RT} \tag{3}$$

with:
Z = pre-exponential factor (min^{-1}) e.g. describing the number of successful collisions of the reaction molecules
E_A = activation energy (J/mol)
R = gas constant (8.314 (J/mol K)
T = absolute temperature (K)

As the activation energy is of interest to achieve knowledge of detailed crystallization kinetics in the range of the measured temperatures it is necessary to derive a specific kinetics function for every investigated polymer. Thus by combining (1-3), convert it into a logarithmic form and assuming a constant conversion at yield, the result is a linear equation that can be used.

In plotting the resulting crystallization times (*ln [Δt_{pc}]*) against the reciprocal of the given isothermal temperature (1/T$_{iso}$) the activation energy for crystallization can be calculated from the gradient of the approximated straight line, Fig. 2.

$$\ln[\frac{d\alpha}{dt}] = \ln[Z] - \frac{E_A}{RT} + m\ln[\alpha] + n\ln[1-\alpha] \qquad (4)$$

$$\ln[\Delta t_{pc}] = -\frac{E_A}{RT_{iso}} + c \qquad (5)$$

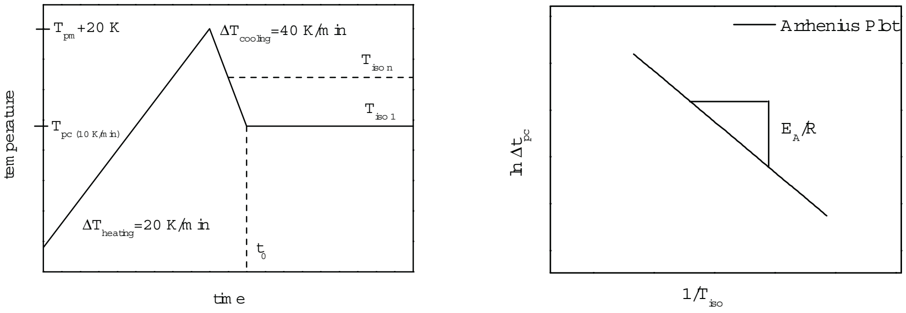


Fig. 2. Schematic plot of the experimental procedure of DSC tests

4.3. SLS Parameter Studies and Component Testing

Having determined the admitted building temperatures in previous thermoanalytical tests, reference specimens can be produced from POM, PE-HD, PP and PA12. For this purpose, tensile bars were built on a modified DTM Sinterstation 2000 following different irradiation strategies. The parameters were varied according to the following formula, until the layers were bonded completely and an optimum in mechanical properties was reached:

$$E_L = \frac{P_L}{v_S \cdot h_S \cdot d_L} \qquad (6)$$

E_L = energy density (J/mm^3)
P_L = laser power (W)
h_S = hatch distance (mm)
v_s = scanning speed (mm/s)
d_L =layer thickness (mm)

Layer bonds and resulting morphologies of the tensile bars' were determined by examining images of microtome cuts taken by a transmitted light microscope. Tensile tests were conducted on the laser sintered parts according to DIN EN ISO 527-1,-2.

5. Results and Discussion

5.1. Thermoanalytical Investigations

By using different cooling rates for DSC measurements it could be shown that crystallization has a high time dependency. Fig. 3 shows that the crystallization starts at higher temperature with lower supercooling of the molten material. Especially the sintering of PE-HD could be influenced significantly, as the difference between melting and crystallization peak is very narrow. The findings presented show that the investigated thermoplastics start to crystallize even before the assumed crystallization temperature is reached, when standard cooling rates of 10 or 20 K/min are used. The range of processing parameters, determined in the standard DSC process, are thus unsuited to serve as the sole processing criteria.

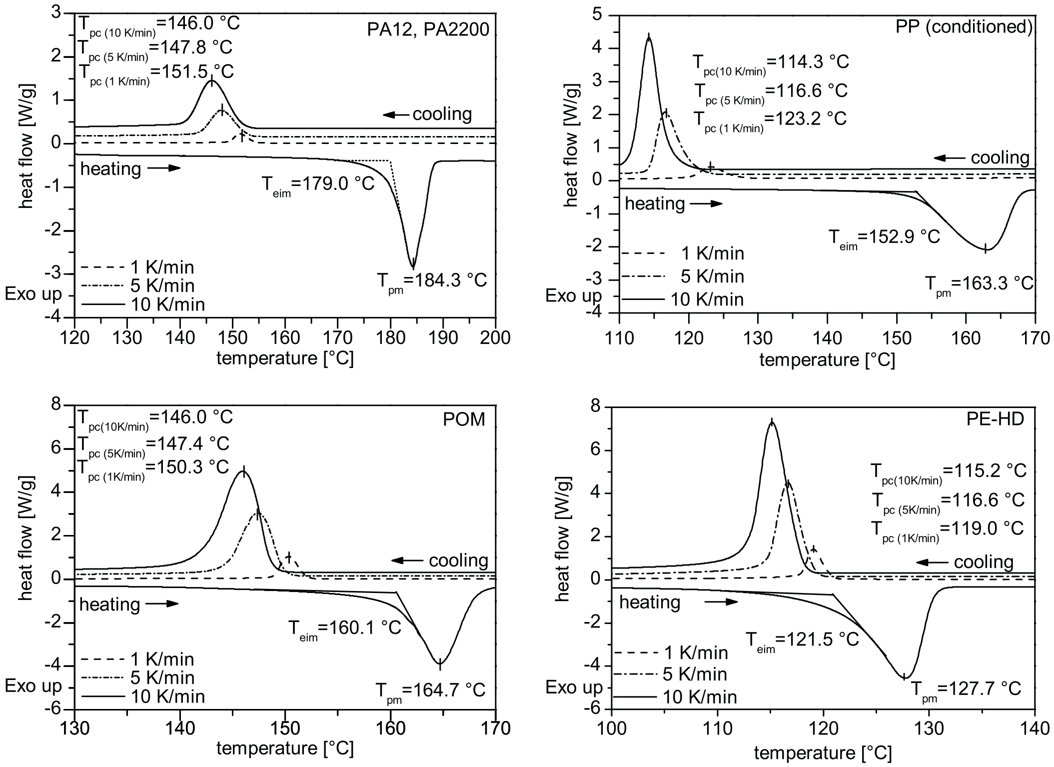


Fig. 3. DSC heating and cooling heat flow curves for different polymers

Due to the fact, that selective laser sintering is a very slow process in which the polymer is kept in a molten state for a long period of time, isothermal measurements were done to simulate a building process. Besides the determination of the building temperature via the difference between crystallization and melting peak in temperature also the available time between phase changes can be measured for different isothermal temperatures. Thus the time-stability of the two-phase area can be analyzed.

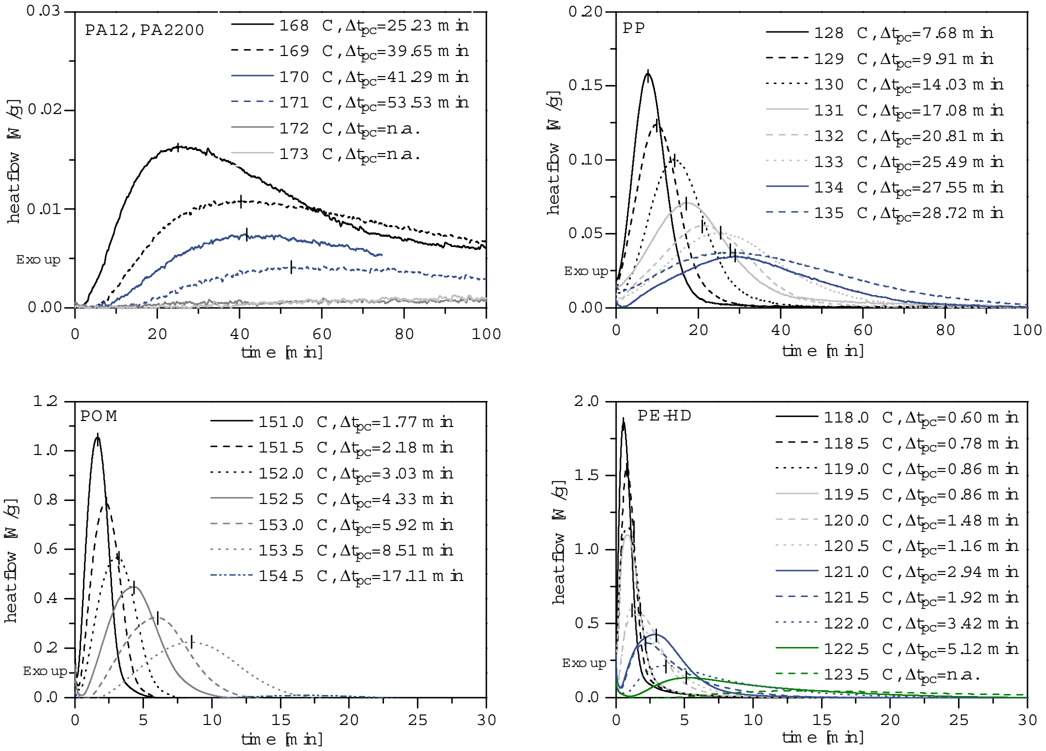
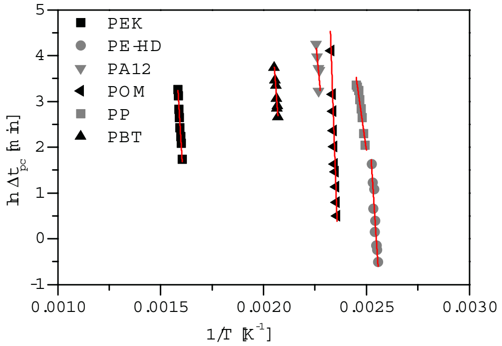


Fig. 4. Isothermal DSC heat flow curves at different temperatures near the crystallization temperatures based on cooling curves



Material	Activation Energy E_A [kJ/mol]
PP	265,0 ± 24,3
PA12, PA2200	395,0 ± 216,2
PBT	521,5 ± 47,0
PE-HD	578,5 ± 70,0
PEK, PEEK-HP3	636,0 ± 21,3
POM	986,7 ± 29,5

Fig. 5. Plot of isothermal peaktimes vs. reciprocal temperatures (left)
calculated activation energies (right)

The isothermal DSC runs illustrate the time until the crystallization peak was reached, Fig. 4. Above the highest shown temperatures no defined crystallization peak could be observed. These are minimum temperatures used for the generation of samples in the SLS process. In general PA12, after pre-drying, is the material that features the latest crystallization point among all examined thermoplastics, which means that above T_{iso} = 172 °C one may assume that there is a two-phase area available over a long period of time for the building process.

Accordingly, to set the building temperature right, it is not sufficient to know the range of possible temperatures determined by DSC heating and cooling curves. For instance, if a low building temperature is set, crystallization may start during layer generation, which typically reveals in the component contour bending upwards. Especially, if new thermoplastics like PE-HD with a narrow range of possible temperatures between melting and crystallization are processed, this can be an unfavorable aspect, as building temperatures need to be regulated accurately.

By means of those isothermal DSC measurements also the activation energy for crystallization was calculated, Fig. 5. The results show that POM and PEEK HP-3 have the highest activation energies. Thus, the gradient for the function describing the phase transformation due to crystallization is the highest in the measured temperature interval. On the other hand, PP and PA12 have the lowest slope and activation energy. Consequently a temperature change (supercooling) near the crystallization temperature is not as severe for the beginning and the overall kinetics of crystallization.

5.2. SLS Parameter Studies and Component Testing

The laser sintering tests were mainly focused on determining the building parameters that permit complete layer bonding, while keeping energy density as low as possible to prevent degradation. The samples have a high density with few pores and defects. Especially the morphology is of high interest to comprehend the processing behavior. Therefore the upper and under surface were analyzed more in detail. Fig. 6 and Fig. 7 present microtome cuts taken from different tensile test bars, sintered at the LKT.

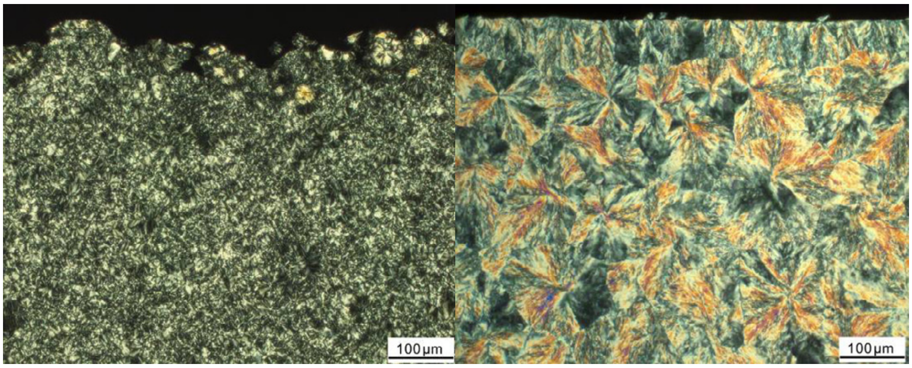


Fig. 6. Transmitted polarized light images taken from the upper surface of microtome cuts made from laser sintered tensile bars of PA12 (left) and POM (right)

As known PA12 parts have molten particles on the interface between part and surrounding powder bed, Fig. 6 (left). In contrast to this known effect POM has no unmolten particles but oriented crystals on the upper surface of parts indicating that crystallization took place before particles of the subsequently applied layer could be molten, Fig. 6 (right). This confirms, the findings of a fast crystallization at little undercooling in isothermal measurements. As some spherulites have a bigger size than single layers and a full bonding of layers was achieved, it can be suggested that the early crystallized interface was remolten. The investigated polyolefin parts show strong interactions between melt and solid particles, Fig. 7. Due to heat flux and low melting viscosity in the first molten layers, surrounding particles are fused together with the tensile bar. This is very distinctive with PE-HD, as the boundary layer is up to more than 200 µm in thickness. Additionally with PP, oriented crystals grow in the bottom regions of the predominantly of β-crystals consisting samples.

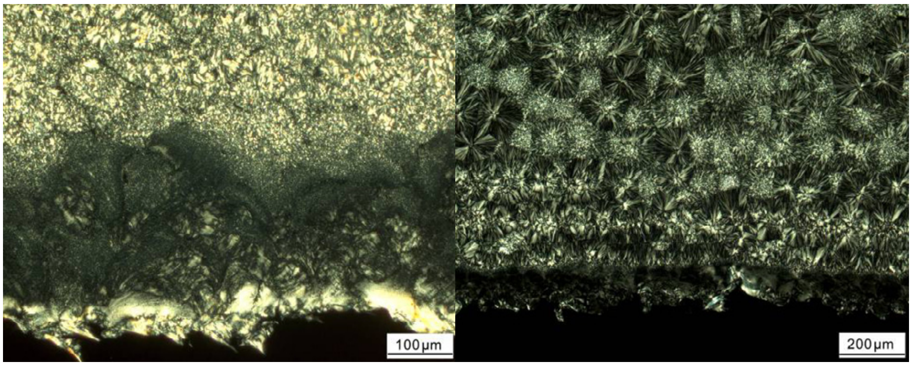


Fig. 7. Transmitted polarized light images taken from the bottom surface of microtome cuts made from laser sintered tensile bars of PE-HD (left) and PP (right)

The specimens produced were tested as to their mechanical properties in a tensile test and compared to each other, Fig. 8. Accordingly, with horizontally built tensile test bars, values of E-modulus as well as tensile stress at break are comparable to expected material values from literature [1]. For all specimens the values of elongation at break, achievable up to now, are clearly below expected values. Apart from the structure resulting from long sintering times, and from the high degree of crystallinity, the poor elongation at break is due to the coarse surface and the residual porosity of parts. Fractures mainly start in the notches on the coarse surface.

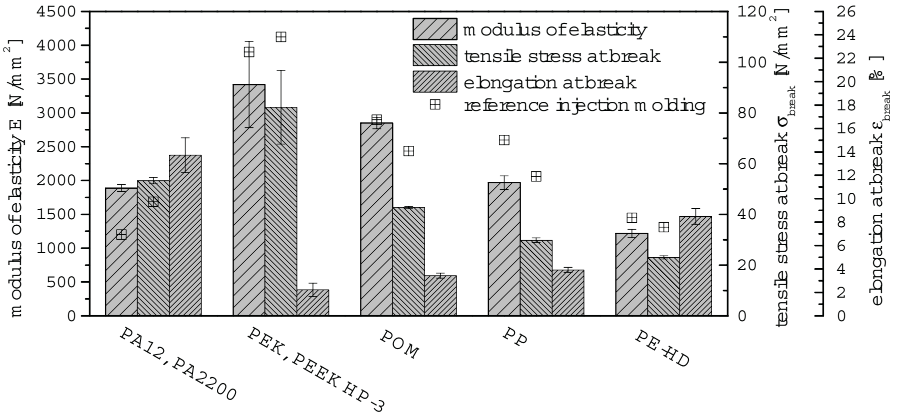


Fig. 8. Mechanical properties of laser sintered tensile bars compared to material specific values from literature [1]

6. Summary and Outlook

It could be shown that it is possible to generate components of thermoplastic materials other than PA12 by laser sintering under consideration of optimized processing parameters. This broader spectrum of usable materials opens up a wide range of applications for the process. Considering process behavior (e.g. time dependent crystallization), the investigated PA12 type certainly is an extremely robust material compared to other investigated polymers. However, thanks to improvements in machine engineering, the potential of other laser sintering powders for commercialization has been stepped up, too. Materials such as polypropylene and polyetherketones are currently entering the market. Apart from the investigations presented in this study, concerned with materials' fusing and crystallization behaviors, other models to describe the processing behavior are growing in importance. They are required to qualify these new materials comprehensively. Especially the existence of the two-phase SLS model has to be studied more in detail in order to know more about the beginning of melting and crystallization but also the kinetics and time-temperature behavior of such processes. By means of direct manufacturing it is necessary to generate parts with constant properties and quality by means of morphology and degree of crystallinity. The thermoanalytical tests pointed out that it will be of high importance to know about the whole built job instead of focusing on single parameters on the upper layer only. Still today's patents in this field just focus on controlling and measuring the current layer instead of looking deeper into z-direction [19-20]. Moreover, it was possible to generate, from the mentioned powders, components with typical basis material properties - with regard to stiffness and strength, whereas fracture behavior was brittle with all the materials under investigation. Finally, there is high potential for further improvements of process-specific measurements techniques and the processing of new polymers.

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