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INVESTIGATION OF THE PARTICULAR CRYSTALLIZATION BEHAVIOUR OF SEMI-CRYSTALLINE THERMOPLASTIC POWDERS PROCESSED BY SELECTIVE LASER SINTERING

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Abstract: *Selective laser sintering is a promissing technology for the direct production of components by means of rapid manufacturing. Currently, the standard thermoplastic powders for selective laser sintering are based on polyamide12. Thus great efforts are made to process new technical thermoplastics like polypropylene or polyether-ketones by selective laser sintering. In this paper the suitability and processing behaviour of thermoplastic powders, by means of melting and solidification are studied, and effects of the process-related isothermal crystallization are presented. Based on thermoanalytical methods, new materials like polypropylene, polyoxymethylene and polyethylene were processed. Subsequently, a correlation between part properties and processing behaviour was derived in order to provide a better understanding of the influencing processing parameters for laser sintering. With these investigations it is now possible to validate thermoanalytical characterization technologies, manufacture components of new materials and expand the knowledge of occuring phase-transitions effects when sintering.*
Keywords: *isothermal crystallization, SLS, new materials*

1. INTRODUCTION AND MOTIVATION

Products made by additive manufacturing have grown in importance, now being much more than mere objects for demonstration. This is one of the reasons why currently many committees, like the ASTM F42 or VDI work intense on new standards for additive manufacturing technologies. One of their major challenges is the reproducibility of part properties achievable in a layer-wise manufacturing process.

Influencing parameters are the use of refreshed powders with varriing properties, transient temperatures in the chamber due to warm-up strategies but also effected by placement of components. Especially the arrangement of stl-files with different volumes in the building chamber is crucial for the overall properties. Fig. 1 shows exemplarly a build job of shells for mobile phones above different volumes. Due to heat transfer of the beneath placed components, the pre-heating of surrounding powder and thus resulting accuracy to size, cristallinity and mechanical properties will be influenced for each shell. Currently, there are new semi-crystalline thermoplastics, e.g. polypropylene (PP) or polyetherketone (e.g. PEEK HP-3) on the verge of entering the market. Additionally, it could recently be shown that other important thermoplastic materials like polyethylene (PE-HD) and polyoxymethylene (POM) can be processed by SLS, too. (Rietzel et al., 2010; Rietzel et al., 2008)

The investigations presented in this paper are focused on studying the effects near phase transitions (melting and crystallization) for different polymers in order to derive an understanding of occurring processes as basis for direct manufacturing in the future. Especially, melting and solidification behaviour must be known because they are of outstanding importance for the laser sintering process. The established model of a quasi-isotherm laser sintering process (Schmachtenberg and Seul, 2002) is in general used as basis for the processing behaviour of polymers. Hence the influences of time-dependent crystallization effects are studied to enhance the existing model.

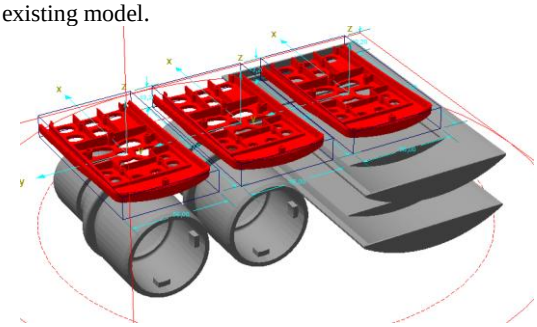

Fig. 1. Different arrangements of data sets in an SLS machine

2. MATERIALS AND METHODS

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 alternative thermoplastic powders. Cryoscopic grinding to a particle size below $d_{3,max}$ = 80 µm was done with POM granules (BASF SE), the generated powder was then mixed with 0.2 wt.-% of Aerosil® (Degussa AG), in order to step up flowability. PE-HD (DuPont, $d_{3,50}$=24-36 µm) and PP (DuPont, $d_{3,50}$=30-45 µm) were provided as powders in spherical geometry. By adding 0.4 wt.-% of Carbon Black® (Degussa AG) the penetration depth of the laser could be limited to approximately 100 µm for PE-HD, as it has poor energy absorption behaviour in the wavelength of the CO_2-laser.

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 are the standard heating and cooling rates, for thermoplastics. By using different cooling rates it could be shown in previous works (Rietzel et al., 2010) that crystallization has a high time dependency and as part generation with laser sintering is a quais-isothermal process,

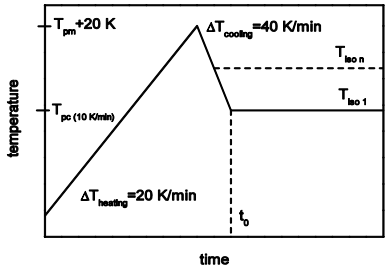

Fig. 2. schematic plot of the experimental procedure of DSC tests

standard measurement technologies are unsuited to sufficiently describe the real process.

The basic 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. The specimens were heated in a defined program according to **Fehler! Verweisquelle konnte nicht gefunden werden.**. The isothermal temperatures (T_{iso}) were determined as temperatures above measureable crystallization in dynamic DSC runs. The heat flows and crystallization times (the time between the beginning of the isothermal measurement t_0 and crystallization peak t_{pc}) were recorded and a model for crystallization kinetics could be derived. For the calculation the common Šesták-Berggren kinetic model for isothermal crystallization was used. (Sestak and Berggren, 1971) In order to describe the change of crystallization rate as a function of temperature, the Arrhenius equation was used for homogeneous kinetics in isothermal processes (ASTM, 2008). Subsequently, the activation energy for crystallization can be calculated from the gradient of the approximated straight line. The gradient describes the influence of temperature shifts on the crystallization.

$$\ln[\Delta t_{pc}] = -\frac{E_A}{RT_{iso}} + c \qquad (1)$$

E_A = activation energy (J/mol)
R = gas constant (8.314 (J/mol K)
T_{iso} = isothermal temperature (K)
c=constant

Having determined the admitted building temperatures in previous thermoanalytical tests, reference specimens were produced from POM, PE-HD, PP and PA12 on a modified DTM Sinterstation 2000 following different irradiation strategies.

3. RESULTS AND DISCUSSION

The time between phase changes was measured for different isothermal temperatures for all polymers and the time-stability of the two-phase area was analyzed. By means of isothermal DSC measurements the activation energy for crystallization was calculated. The results in Tab. 1 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, e.g. by adding colder layers of powder, near the crystallization temperature is not as severe for the beginning and the overall kinetics of crystallization, which means that there is a two-phase area available over a long period of time for the building process.

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

Tab. 1. Calculated activation energies

Fig. 3 presents microtome cuts taken from the upper regions of PA12 and POM tensile test bars, sintered at the LKT. Both images show that big spherulites grow due to the isothermal conditions but especially in the interface between surrounding powder and molten areas both materials are significantly different. PA12 parts have molten particles on the interface between part and surrounding powder bed acting as nuclei, Fig. 3 (left). In contrast to this effect with POM no unmolten particles are visible, but oriented crystals on the upper surface of the cross section indicating that crystallization took place before particles of the subsequently applied layer could be molten, Fig. 3 (right). This confirms, the findings of a fast crystallization at little undercooling in isothermal measurements. All sintered samples have a high density with few pores and defects.

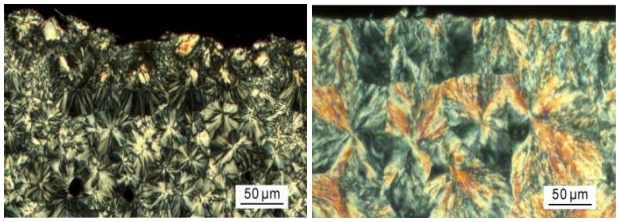

Fig. 3. Microtome cuts of laser sintered tensile bars made from PA12 (left) and POM (right)

4. CONCLUSION AND OUTLOOK

Considering process behavior (e.g. time dependent crystallization), the investigated PA12 type certainly is an extremely robust material compared to other investigated, faster crystallizing polymers like PEEK HP-3 and POM. However, thanks to improvements in machine engineering, the potential of other laser sintering powders for commercialization has been stepped up, too. The results show that the existence of the two-phase SLS model can not be generally transferred to all types of polymers. Further research will focus on melting and crystallization but also the kinetics and time-temperature behavior of phase-changes. For the aim 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 surface of the building chamber only. Still today's patents in this field just focus on controlling and measuring the current layer instead of looking deeper into z-direction (Chung Mark and Allanic, 2004). Finally, the presented concept is a first approach to predict and simulate properties of laser sintered components.

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