Available online at www.sciencedirect.com

ScienceDirect

Physics Procedia 83 (2016) 981 – 990

Physics Procedia

9th International Conference on Photonic Technologies - LANE 2016

Laser-high-speed-DSC: process-oriented thermal analysis of PA 12 in selective laser sintering

Lydia Lanzl[a,b,*], Katrin Wudy[a,b], Maximilian Drexler[a,b], Dietmar Drummer[a,b]

[a]*Collaborative Research Center-Additive Manufacturing (CRC814), Am Weichselgarten 9, 91058 Erlangen, Germany*
[b]*Lehrstuhl für Kunststofftechnik, Am Weichselgarten 9, 91058 Erlangen, Germany*

Abstract

In the Selective Laser Sintering process very high heating rates occur due to the melting of the material by a laser. Extreme scanning rates could not be measured by conventional thermal analysis methods, since typical heating rates for DSC (differential scanning calorimetry) are between 5-20 K min-1. By using a Laser-High-Speed-DSC, a self-developed combination of a Flash-DSC and a fitted laser head, the sample is directly heated by a CO2 laser like in the SLS process. These experiments allow a process-oriented thermal analyzation of the material. In this paper, the set-up and function of this new measuring method is introduced. Furthermore, the reliability of the measurements is evaluated by statistical design of experiment methods. By using this new measuring method, the time-dependent melting behavior of the polymer can be analyzed. Moreover, sample temperatures and heating rates dependent on laser exposure times can be quantified.

Peer-review under responsibility of the Bayerisches Laserzentrum GmbH

Keywords:

1. Motivation and state of the Art

Selective Laser Sintering (SLS) is the method of choice for highly individualized parts, which are produced by additive manufacturing (AM) for small batch production due to the good layer-to-layer connection compared to other AM techniques (Wohlers 2010). Therefore, the production of reproducible parts is of great importance, so a fundamental understanding of the process is mandatory. In Selective Laser Sintering very high heating and cooling

* Corresponding author. Tel.: +49-9131-8529736 ; fax: +49-9131-8529709 .
E-mail address: lanzl@lkt.uni-erlangen.de

Peer-review under responsibility of the Bayerisches Laserzentrum GmbH
doi:10.1016/j.phpro.2016.08.103

rates are generated in the building process while the actual cross section of the part is melted by a CO_2-laser. By heating the material with a laser, a temperature of the molten mass is reached that is much higher than the melting

Nomenclature

A_L	Area of the laser beam
d_f	Focus diameter
E	Energy density
P_L	Laser power
t_L	Laser impact time

temperature of the material (Schmid 2015). In contrast to that, the cooling rate during the consolidation sub-process is tending to zero. Since the properties of polymers are to a great extent time- and energy dependent, melting kinetics are essential in order to understand the behavior of a material during the process. The interval of the melting peak temperature and the crystallization temperature determines the process window of SLS, but it is dependent on the heating- and crystallization rate (Alscher 2000). Therefore, thermal analysis is important to acquire knowledge of the behaviour of a material under certain heating and cooling rates. Up to now, the boundary conditions of the SLS process have not been seizable by conventional thermal analysis methods. By using a Laser-High-Speed-DSC, a SLS process can be imitated in a small scale, since the sample is directly heated by a laser. So the heating rates are similar to the process and freely configurable dependent on the laser exposure time and laser power. In this paper, the new measuring method, which allows a process-oriented thermal analysis of the polymer in the SLS process, is introduced and the performance is tested on its reproducibility. The new system makes the quantification of sample temperatures and heating rates possible, which are achieved in the process. The Laser-High-Speed-DSC is a unique self-developed and therefore not commercial measuring method, so it has not been possible to conduct a process-oriented thermal characterization so far. Investigations of the commercially available Flash-DSC-1 have shown that reorganization phenomena and meta-stabilities of the polymer can be measured (Mathot, Pyda et al. 2011). If the heating rate is low, meta-stable structures of polyamides tend to form stable structures, e.g. thick lamellae, due to the long period of melting time. At an increased heating rate, a recrystallization process cannot take place anymore (Ehrenstein, Riedel et al. 2003). The heating rate has an influence on the temperature interval of the melting point and the crystallization point. Also the formation of the melting and crystallization peak is influenced although the period of time of the melting or crystallization exceeds the actual transition temperature. A reason for that is the higher mobility of polymer chains with an increasing temperature and connected to that the decrease of partial valence forces (Alscher 2000). Moreover, it was demonstrated that a variation of the cooling rate drastically influences the crystallization behaviour of polyamide 12. Hereby, a decrease of the crystallization peak with an increasing cooling rate can be observed. Also the peak area is decreased, which implies lower crystallinity. During the measurement, recrystallization effects are avoided because of the very fast heating rates so that a realistic material behaviour can be imitated (Drexler, Wudy et al. 2015). The formation of lamellae and the lamella thickness distribution is influenced by the crystallization rate in a great extent (Alscher 2000).

2. Experimental

2.1. The instrument

2.1.1. The Laser-High-Speed-DSC

For this special setup of the Laser-High-Speed-DSC a combination of a commercial Flash-DSC 1 from Mettler Toledo and an integrated laser head is used, see Fig. 1 (a). Typical heating rates of the commercial Flash-DSC-1 (Mettler Toledo) range from 30 – 2 400 000 K min-1, while cooling rates are between 6 – 240 000 K min^{-1}. The Laser-High-Speed-DSC allows a thermal observation under a laser based energy input. Here, a freely configurable CO_2-laser is used in order to melt the polymer sample. Thermal processes in the sample can be observed while the sample is exposed to laser radiation. This means that a SLS process in a very small scale is imitated while it is thermally analyzed. At first, the laser beam is deflected by a mirror system and is thus targeted onto both the sample

and the reference site to the same degree, see Fig. 1 (b). An aperture allows a deflection of the laser beam either to the reference site or to the sample site, which is necessary for the laser adjustment. Thereby, the same laser power on both sites can be guaranteed. Measuring the temperature difference between the sample and reference site, the heat flow can be calculated.

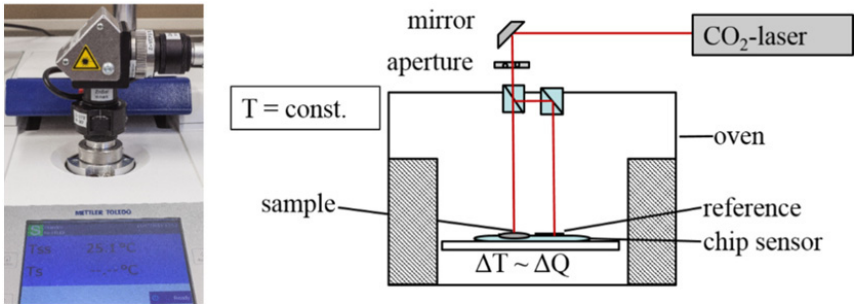


Fig. 1. (a) Flash-DSC-1 with the fitted laser head; (b) Schematic setup of the Laser-High Speed-DSC.

2.1.2. Chip sensor

For this measurement a MultiSTAR UFS 1-Sensor is used, a twin sensor, which is based on the MEMS (Micro-Electro-Mechanical Systems) sensor technology, see Fig. 2. It has 16 thermal elements, which are mounted on a silicon carrier with an electric connection on a ceramic carrier.

The twin sensor contains a sample and a reference site membrane that are made of silicon-nitride/oxide with a thickness of 2 µm and an area of 1.6 mm x 1.6 mm. The sensor is inserted in a silicon frame. The thin membranes guarantee high temperature accuracy and low power need. Both contain two resistance heaters, which generate the temperature program. The smaller heating element conducts the compensation controlling (dynamic compensation controlling). Eight thermopiles are placed symmetrically around the sample and the reference site, whereby the temperature is measured in respect to the silicon frame serving as a heat sink. (Poel, Istrate et al. 2012).

The diameter of the sensor area is 0.5 mm for each site, but the heating and cooling takes place only at about one fifth of the sensor area. An aluminum coating allows a homogenous temperature distribution (Mathot, Pyda et al. 2011). The melting film of the sample comprises an area of about 0.015 mm² depending on the amount of the particles used for the sample preparation. The value of 0.015 mm² is valid for a sample amount of four particles.

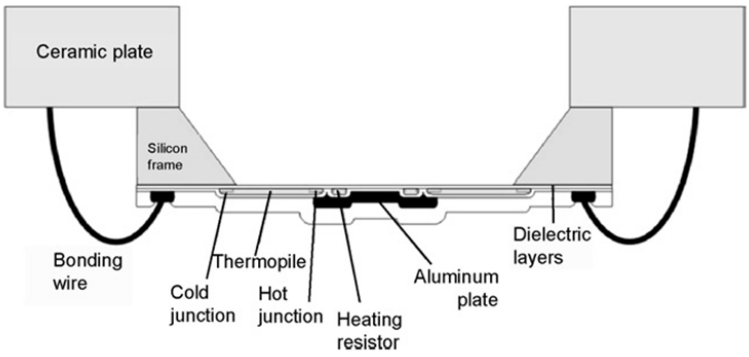


Fig. 2. Schematic cross-section of the chip sensor (Mathot, Pyda et al. 2011).

2.2. Sample preparation

To realize such high heating and cooling rates, the mass of the sample has to be minimized. No pan or sample holder is used, the sample mass ranges in between µg and ng, respectively, so the sample is not weighable. High sample masses used in conventional DSC-measurements (~5-10 mg) compared to the very low sample amount for High-Speed-DSC lead to a thermal inertia at high heating rates and to low changes in temperature of the sample material (Drexler, Wudy et al. 2015). For taking a sample, 3-4 particles of a laser sintering powder (here: PA 2200) are directly placed on the middle of a sensor chip using a hair that adheres the particles due to electrostatic effects. The very small scales at sample handling make a microscope necessary. The Flash-DSC runs one heating (heating rate: 20 K s^{-1}) and cooling cycle (cooling rate: -20 K s^{-1}) first in order to melt the particles, so that a thin molten film covers the sensor for maximizing the area of thermal transfer (Mathot, Pyda et al. 2011).

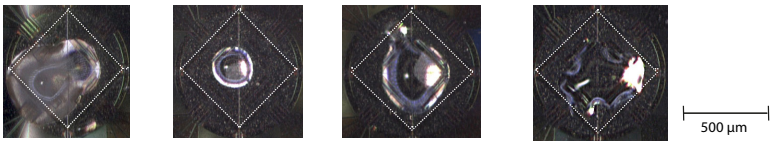
The used material for this experiment is polyamide 12, type PA 2200 by EOS GmbH, Krailling, Germany. PA 2200 is a standard material for selective laser sintering and is therefore the most understood material in terms of SLS. The focus of the following measurements is to figure out the repeatability and performance of the Laser-High-Speed-DSC. Therefore, four different chip sensors are used, with the laser head and chip sensors are each mounted twice. One chip sensor (chip 3) contains twice as much sample than the other two sensors in order to find out any influences of the sample amount, the sample load of chip 4 is about thrice the sample amount of chips 1 and 2.

Table 1 shows an overview of the chips and the amount of sample, e.g. the number of particles used for the sample melting film. Chip 1 (27374) shows a large coverage of the sample, being the result of an unsymmetrically melting of the sample. However, the largest part of the sample lies outside the measuring area. Therefore, the number of particles in the relevant chip sensor area is approximately 3-4.

The focus diameter d_f is 500 µm and covers the whole sample area.

Table 1. Chip sensors used with the containing sample amount.

	Chip 1	Chip 2	Chip 3	Chip 4
Sample amount (number of particles)	3-4	3-4	7-8	10-11



2.3. The measurement

The temperature program, see Fig. 3, is set to process conditions, so that the laser shot is conducted at working temperature, e.g. 170 °C . The first step (1) is to hold the temperature at 40 °C, followed by a heating step up to the temperature of the building chamber (170 °C) with a heating rate of 1000 K s^{-1} (2). In the third phase (3), the temperature of 170 °C is constant. During this period of time, the laser is manually fired with various impact times by a control system. Afterwards, the sensor temperature is cooled down to 20 °C (4,5) with a rate of -100 K s^{-1}. For defined initial conditions the sample is melted and crystallized in a last step (6). The values of the heating and cooling rate were chosen for these first measurements, since melting and crystallization effects could be observed properly. The heating and cooling rate of further investigations will be further converged to process conditions.

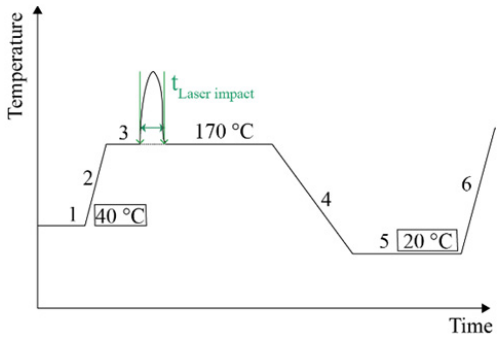


Fig. 3. Temperature program of the Flash-DSC-1.

The initial cooling of the sample is passive, due to the end of the laser shot, depending on the laser impact time. The cooling of the sensor temperature is carried out by an external cooler. The measuring chamber is purged with nitrogen, in order to avoid thermal oxidation of the polymer sample.

Both, the sensor and the sample are heated by a CO_2-laser. The laser is pulsed and has a frequency of 10 kHz. Depending on the material, absorption and laser power, the temperature of the sample is measured and the heating rates are calculated. Depending on the laser impact time and the laser power, the sample temperature as well as the heating rate, which is the temporal derivation of the change in temperature, can be calculated. An example of the analyzation of the sample temperature and heating rate is shown in Fig. 4. The maximum sample temperature is evaluated by the peak value, hence the maximum of the heating rate is the maximum gradient of the change in temperature. Mathematically seen, the cooling point, e.g. the end of the laser impact time, is the inflection point in the display of the heat flow curve.

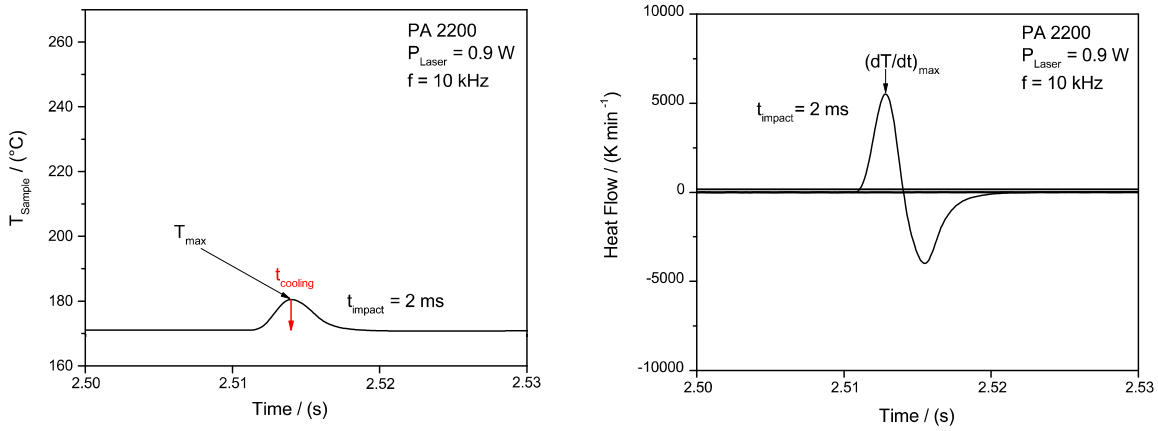


Fig. 4. Analyzation scheme of maximum sample temperature (left) and heating rate (right).

2.4. Design of experiment

The repeatability of two mountings of each chip sensor is evaluated as well as the influence of the sample amount, see Table 1. For that, the sample temperature and heating rate, dependent on the set parameters is analyzed. The frequency is f = 10 kHz in all cases. The area of the focus beam is approximately A_L= 0.2 mm². With equation (1) the energy density E can be calculated.

$$E = \frac{P_L \cdot t_L}{A_L} \tag{1}$$

The design of experiments is shown in Table 2. Three single measurements were conducted per parameter setup (n=3). The sample amount of every chip sensor was varied as shown in Table 1.

Table 2. Varied Parameters (P_L: laser power, t_L: laser exposure time).

Number of chip sensors	4
Number of mountings per chip sensor	2
P_L [W]	0.6, 0.9, 1.75
t_L [ms]	1, 3, 6, 9

Wegner (Wegner 2015) describes an energy density of E = 0.035 J mm^{-2} as the standard value in industrial application. The parameters as shown in Table 2 were chosen in order to test the lower and upper boundary of industrial used energy densities. The parameter setup of P_L = 0.6 W and a laser impact time of t_L = 1 ms results in an energy density of E = 0.003 J mm^{-2}, P_L = 1.75 W and t_L = 9 ms equals E = 0,079 J mm^{-2}. Comparable to the standard energy density of E = 0.035 J mm^{-2} is the parameter setup of P_L = 0.9 W and t_L = 6 ms, which results in E = 0.027 J mm^{-2}.

3. Results and discussion

3.1. Determination of temperature

For each chip sensor the sample temperature dependent on the laser power and the laser impact time is measured. The results for chip 1 and 2, which both contain 3-4 particles as a sample, are shown in Fig. 5. With increasing laser power and laser impact time a significant rise of the sample temperature can be seen, which is due to a higher energy input. The single repeats of measurements (n=3) within one mounting of a sensor chip show a high reproducibility. The comparison of the lower laser power curves, e.g. 0.6 W and 0.9 W, of chip 1 and 2 as well as the comparison of two mountings of one chip sensor lead to repeatable results. Nevertheless, the average temperature of chip no. 27375 at P_L=1.75W and impact time of 9 ms is 20% higher than the temperature of chip 1 at the same parameter setup.

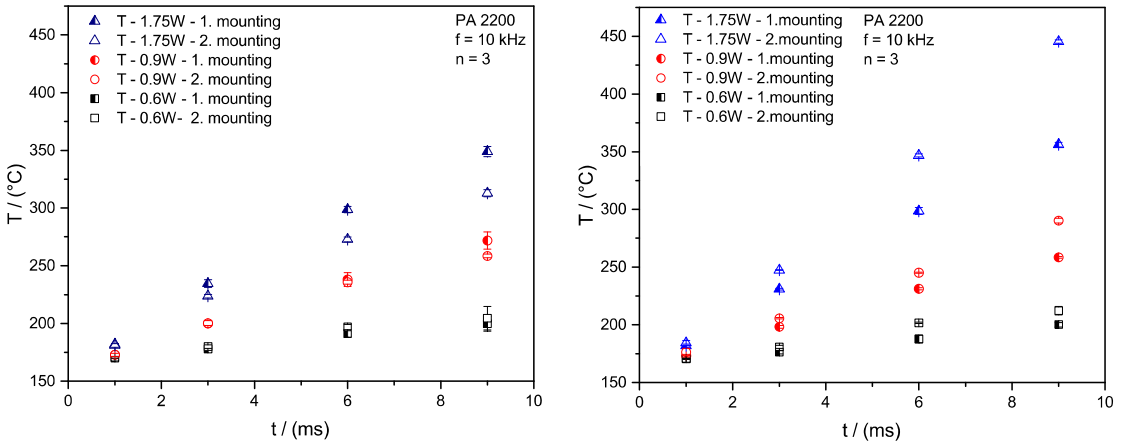


Fig. 5. Sample temperatures of chip 1 (left) and 2 (right) dependent on laser impact time t and laser power P_L.

Also the variance at that parameter setup is the highest, which might be due to the fact that the sample amount of chip 1 is nevertheless higher than chip 2, because of the unsymmetrical melting. So the low sample amount of chip 2 might lead to an increasing warming of the sensor, because it cannot absorb the energy completely. The maximum error of chip 1 is 7 %. The large variance at a parameter setup with a high energy input might also be a result of the sample's warmth imbalance, e.g. the energy input is higher than the energy release or vice versa.

The yielded temperatures of 350-400 °C might have an influence on material degradation, which could be checked by driving an adjacent DSC-curve. Changes in the crystallization temperature or the melt temperature reveal material degradation.

The results of the temperature determinations of chip 3 and 4, which contain two (chip 3) and three times (chip 4) the sample amount of chip 1 and 2, respectively, are shown in Fig. 6.

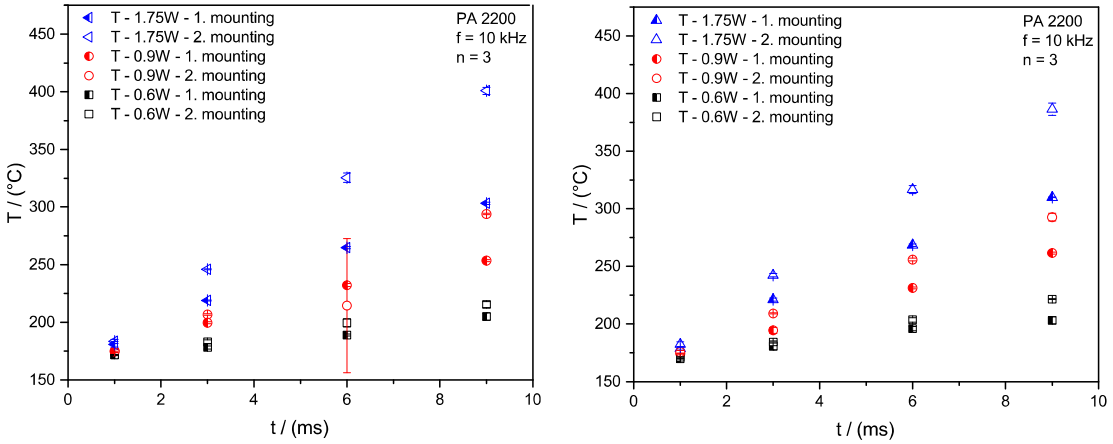


Fig. 6. Sample temperatures of chip 3 (left) and 4 (right) dependent on laser impact time t and laser power P_L.

The average temperature results of chip 3 and 4 are consistent to the results of chip 1 and 2. An increasing laser power and laser impact time leads to a higher sample temperature, whereby the variance also increases. The maximum error of chip 3 is 19 % and 15 % of chip 4. An influence of the sample amount cannot be seen. The comparison of the average temperatures dependent on the laser power and impact time of chips 1 to 4 is represented in Fig. 7. This diagram shows that temperatures up to 350 °C are yielded with the stated parameters.

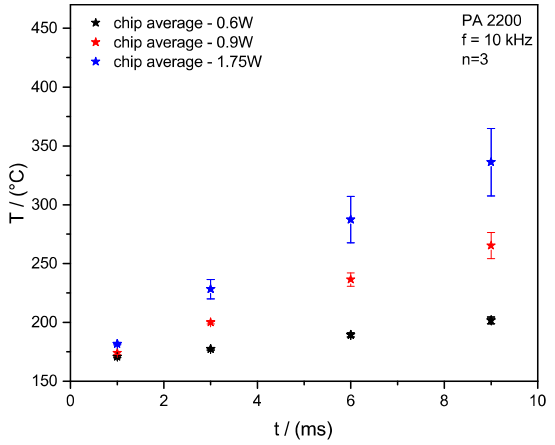


Fig. 7. Comparison of the average temperatures of chip 1-4 dependent on the laser impact time and laser power P_L.

In former investigations, Wegner (Wegner 2015) measured a maximum melt temperature of about 300 °C at an energy density of E = 0.044 J mm^{-2}. In the Laser-High-Speed-DSC measurements as shown in Fig. 5-7 a temperature of approximately 275 °C is reached. This indicates that the measured temperatures by the Laser-High-Speed-DSC lie within a realistic magnitude of order.

The higher the energy input, the higher is the uncertainty of the determined values. The comparison of the average values of the four chip sensors leads to a maximum error of 8.5 %.

There is a temperature dependence of the optical properties in the melt, which leads to a change of absorption, reflection as well as transmission. The beam-material-interaction is essential in the selective laser sintering process. So if the transmission is increased, more energy will be transferred through the actual material layer onto deeper powder layers in the process (Schmid 2015). Analogously, it is not certain how much energy is absorbed in the sample material in the Laser-High-Speed-DSC experiment and to which extent the laser beam is directly transferred on the sensor and leads to a warming there. The experimental setup of the Laser-High-Speed-DSC does not allow a determination on bulk goods due to the low sample amount and the needed adherence on the chip sensor. Another reason for the uncertainty of the values are interferences on thin layers. The coherent path of rays of the laser beam is first deflected on the melting film of the sample and then on the sensor. This results in superposition or extinction of the path of rays, respectively.

3.2. Determination of the heating rate

The temporal derivation of the change in temperature is the heating rate, which can also be calculated by using the Laser-High-Speed-DSC.

The heating rates that are measured with chip sensor 1 and 2 are shown in Fig. 8.

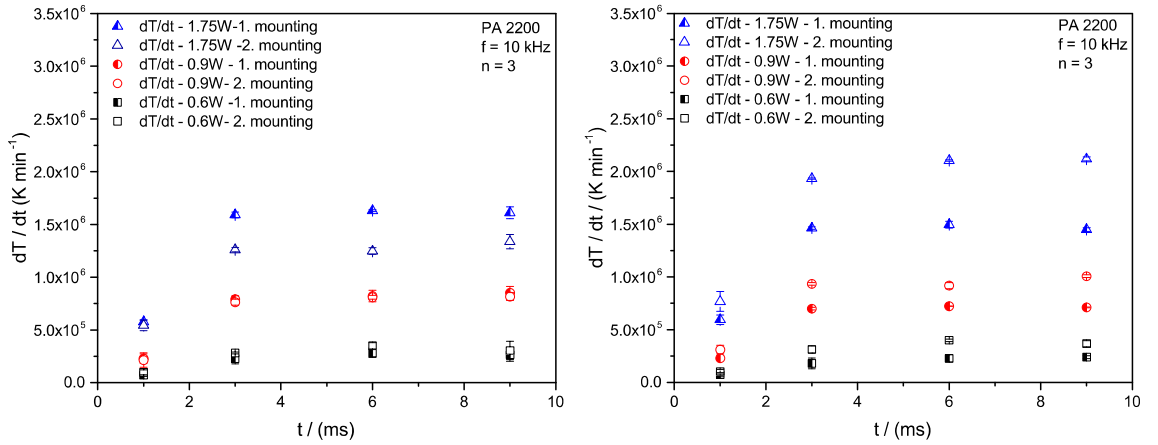


Fig. 8. Heating rates measured by chip 1 (left) and 2 (right) dependent on laser impact time t and laser power P_L.

The results of the determination of the heating rates show an increase from an impact time of t = 1 ms to 3 ms. A longer impact time does not lead to a further increase, but to a saturation instead. A comparison of chip 1 and 2 shows reproducible results for the curves of P_L = 0.6 and 0.9 W. A saturation value of $8*10^6$ K min^{-1} is reached at P_L = 0,9 W in both cases. The values of P_L = 1.75 W of chip 2 are about 16% higher than the ones of chip 1. Also the variance of chip 2 at 1.75 W is much larger in comparison to chip 1 and to lower laser power within the same chip. The maximum error of chip 2 is 26 %.

A further comparison with chip 3 (number of sample particles = 7-8) and chip 4 (number of sample particles = 10-11) show the same average saturation value as chip 1 at P_L = 1.75 W at around $1{,}5*10^6$ K min^{-1}, with a still considerable error. The maximum error of chip 3 is 35 % and of chip 4 25%.

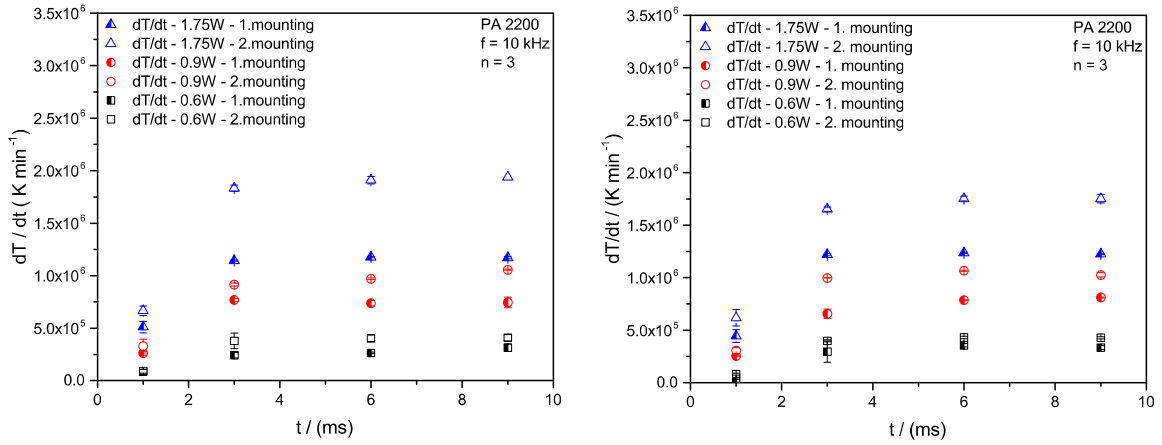


Fig. 9. Heating rates measured by chip 3 (left) and 4 (right) dependent on laser impact time t and laser power P_L.

The values of lower laser powers show a high reproducibility. The high values of the heating rates of chip 2 are results of the low sample amount, since the energy input is higher. Recapitulatory, the heating rates rise with increasing laser power and go over to a saturation level at a laser impact time of t_L = 3 ms, what can be observed in the comparison of the average values of chip 1-4 in Fig. 10.

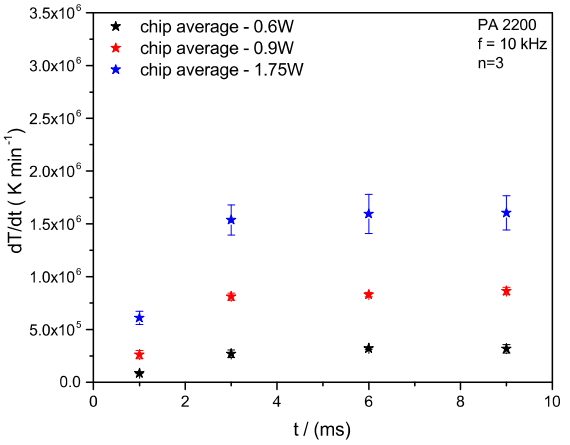


Fig. 10. Comparison of the average heating rates of chip 1-4 dependent on the laser impact time and laser power P_L.

The calculated heating rates make a statement how fast the material in the SLS process is heated while it is exposed to laser light. So the heating rate is dependent on the laser load. Since the properties of polymers are very sensitive to time- and energy based processes, the estimation of acquired heating rates is essential to understand the material's behaviour and hence the parts' properties. Drummer et al. (Drummer, Drexler et al. 2014) proved that with an increasing heating rate the surface temperature also increases. The reason for this is a heat accumulation on the surface leading to a decrease of the time for heat transfer to the surrounding powder bed in the process. Analogously, with an increasing laser impact time the energy cannot be transferred into the sample, but accumulates on the surface instead and leads to a saturation after t_L = 3 ms.

4. Summary and Outlook

The experimental setup of the Laser-High-Speed-DSC is introduced, which allows a process-oriented thermal characterization of materials used for the selective laser sintering process. A combination of a commercial Flash-DSC-1 and a freely configurable laser imitate the SLS process in a very small scale, where the sample temperature and heating rate dependent on the laser parameter set can be measured.

In this paper, the performance and the reproducibility of first measurements of this new and unique method are tested. It could be shown that with an increase of the laser impact time and laser power, the sample temperature increases. However, the error at parameter setups which are responsible for a high energy input is still high.

Possible heating rates that might be achieved in the process while the material is exposed to laser light can be calculated. A saturation after a laser impact time of t_L = 3 ms takes place at all tested laser powers. The variation of the used sample amount leads to the assumption that a low sample amount leads to a warming of the sensor in a greater extent due to the higher transfer of the laser beam through the sample. Also interferences on thin layers might occur. Nevertheless, the Laser-High-Speed-DSC performs as a reproducible method for thermal values that occur in the SLS process. Yet, no measurements on bulk goods are possible, but only particle-wise.

Perspectively, the influence of the layer thickness of the sample will be tested in order to achieve a full absorption of the laser energy in the material. This will be conducted by the application of more powder particles on the existing sample melt film. Furthermore, the laser parameters and the temperature program of the Flash-DSC will further be approached to process conditions. The plausibility of this new method will be investigated by the comparison of the results with process simulations and measurements conducted in the real SLS process in the laser sintering machine. At last, the viscosity in the range of the measured temperatures will be investigated.

Acknowledgements

The authors want to thank the German Research Foundation (DFG) for funding Collaborative Research Center 814 (CRC 814), sub-project A3.

References

Alscher, G. (2000). Das Verhalten teilkristalliner Thermoplaste beim Lasersintern. Aachen, Universität Essen.

Drexler, M., et al. (2015). "Einfluss des Pulverauftragsprozesses auf den selektiven Strahlschmelzprozess thermoplastischer Kunststoffe." RTeJournal-Fachforum für Rapid Technologie 2015.

Drummer, D., et al. (2014). Derivation of heating rate dependent exposure strategies for the selective laser melting of thermoplastic polymers. 30th International Conference of the Polymer Processing Society, Cleveland.

Ehrenstein, G. W., et al. (2003). Praxis der thermischen Analyse von Kunststoffen. München, Carl Hanser Verlag.

Mathot, V., et al. (2011). "The Flash DSC 1, a power compensation twin-type, chip-based fast scanning calorimeter (FSC): First findings on polymers." thermochimica acta 522(1-2): 36-45.

Poel, G. V., et al. (2012). "Performance and calibration of the Flash DSC 1, a new, MEMS-based fast scanning calorimeter." Journal of Thermal Analysis and Calorimetry 110(3): 1533-1546.

Schmid, M. (2015). Selektives Lasersintern (SLS) mit Kunststoffen. München, Carl Hanser Verlag GmbH & Co. KG.

Wegner, A. (2015). Theorie über die Fortführung von Aufschmelzvorgängen als Grundvoraussetzung für eine robuste Prozessführung beim Laser-Sintern von Thermoplasten, Duisburg, Essen, Universität Duisburg-Essen, Diss., 2015.

Wohlers, T. (2010). Wohlers Report 2010 - Additive Manufacturing - State of the Industry. Fort Collins, Colorado, Wohlers Associates Inc.