Temperature Dependent Optical Properties of Polymers as a Basis for Laser Process Modeling

Bernd Keller, Rolf Pfeifer, Wei-Nien Su, Peter Eyerer
Institute of Polymer Testing and Polymer Science, IKP - University of Stuttgart

Abstract

The knowledge of laser absorption is essential to describe the behavior of polymers in different laser processes, i.e. SLS, LOM, etc. By means of transmission IR-spectroscopy a method for measuring temperature dependent penetration depths (absorption length) of polymers, especially at a wavelength of 10.6µm (CO_2-Laser), is developed. Results for the laser sintering materials polystyrene (PS), nylon 11 (PA 11), nylon copolymer (CoPA) and polyethylene terephtalate (PET) are presented. It is detected that the absorption length of polymers will increase or decrease significantly dependent on temperature. This paper will point out simplified methods based on the one dimensional heat transfer equation with volume heat source to set the processing parameters i.e. for the SLS process. The calculations correspond with the measured data.

1 Introduction

Optical and thermal properties are the most important parameters to characterize polymers for laser processing and even determine the applicability of some special applications, i.e. for selective laser sintering. In this work, a method for measuring temperature dependent absorption length of polymers, especially at a wavelength of 10.6µm (CO_2-Laser), will be explored by means of transmission IR-spectroscopy. The temperature dependent absorption coefficient, which is in addition to the thermal properties the decisive material property, permits the prediction of the processability of the polymer in laser sintering. On the basis of the thermal conductivity equation, simplified work curves will be estimated to derive significant processing parameters which will be compared with experimental results. The obtained experimental results of the IR-spectroscopy will be used in the calculations.

2 IR-spectroscopy

Most of the relevant thermal properties (phase change-T_g, T_m, T_z; specific heat capacity-c_p; thermal conductivity-λ; thermal diffusivity-κ and coefficient of thermal expansion) can be determined by standardized testing methods. Optical properties like absorption rate and penetration depths of electromagnetic waves depend on the structural constitution of aliphatic macromolecules. In this case, no direct reliable measurement system is known and the related issues has been less discussed. A device is required to determine the interaction between light, electrons, atoms and molecules. Transmission IR-spectroscopy is suitable to measure eigenfrequencies of atoms in the range of 10^{12} to $3*10^{14}$ Hz (IR). With the knowledge of the position of the „absorption bands in the frequency spectrum“ one receives a so-called fingerprint of the polymer. The extinction which depends on the functional groups of the polymers and the amount of molecules (sample thickness) could be measured by transmission IR-spectroscopy. The quantitative absorption spectroscopy is defined by the Beer-Lambert law:

$$I = I_0 \cdot \exp\left(-\varepsilon \cdot c \cdot d\right), \qquad (1)$$

where I the transmitting intensity, I_0 the entering intensity, d the sample thickness, c the coefficient of the relative density (for dense films c=1) and ε the extinction coefficient. The exponent εd is the measured extinction E. The absorption coefficient a is given by $a = \log e^{-1} \cdot \varepsilon$. The optical penetration depth, also called absorption length l_a, is defined as:

$$l_a = \frac{1}{a}, \qquad (2)$$

and represents the penetration depth in a workpiece where the radiation intensity decreases at 1/e of the entering intensity I_0. The absorption quotas A of the polymers were measured using a diffuse reflexion spectroscopy device. The absorption quota A was found to be above 95% of the entering intensity and varies only slightly for the different polymer powders.

3 Experiments of measuring temperature dependent absorption lengths

The results will help explain the different processability of polymer powders. In addition, the obtained absorption length is an important property to understand the absorption mechanism in polymers by irradiation of CO_2-laser and will be used the later calculations.

3.1 Preparation of polymer films and measuring device

To estimate the extinction- and absorption coefficients with IR-spectroscopy, the transmittance of irradiation on polymer films must be measured. Solid parts (50x30x5mm) are produced by injection molding of the polymer sintering powders and will be subsequently cut into polymer films of 40µm, 80µm and 160µm thickness using a microtome. The temperature history and the influence of moisture were eliminated by tempering the films for 10 min. (PA 11: 160°C, CoPA: 70°C, PET: 160°C) and cooling gradually down to the room temperature. The films were positioned in a temperature cell (max. T=600°C) and adjusted in the envelop between IR-detector and IR-bulb. During measurement the cell was floated with inert gas (Argon) and thermocouples were used to control the temperature.

3.2 IR-Spectra of polymers

Fig. 1 points out an example of a PET-spectrum with characteristic bands of some vibrational forms. The wavenumber of the CO_2-laser ($\nu = 943.4 cm^{-1}$) is marked with a line. The corresponding film thickness is $d = 80 µm$. An exact determination of the vibrational systems responsible for the absorption of the CO_2-irradiation is not possible as a result of superposition of bands.

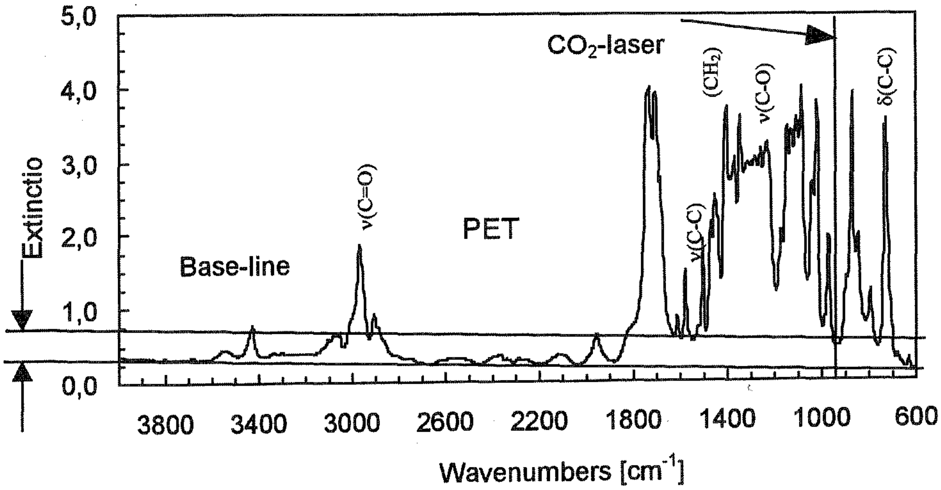


Fig. 1: IR-Spectrum of the sintering material PET at room temperature including the construction of the base-line to determine the extinction E

In this case, the extinction for the wavenumber of the CO_2–laser will be determined by the base-line method. The base-line will be constructed by tangentially connecting two minima of the extinction curve. These two minima have to be two sections of the extinction curve, where there are no intensive bands of vibration. This is a requirement to determine temperature dependent extinctions and as a result to calculate the temperature dependent optical penetration depth. Experiments show that every investigated sintering material has some wavenumber ranges, so-called windows, where the extinction is independent of the temperature and remains at a constant level. The distance between the intersection points of the base-line and the detected IR-extinction line with the plummet at $\nu = 943.4\text{cm}^{-1}$ is the extinction E.

3.3 *Determination of absorption length*

According to the extinction E from the IR-spectrum, the extinction coefficient ε can be obtained by division with the corresponding film thickness d. The absorption length are calculated according to equation (2).

Fig. 2 indicates the calculated absorption lengths of different sintering materials as a function of temperature. Deviations for other film thicknesses are in the range of 10% to 15%. For PA 11 and CoPA which have a similar IR-spectra, the temperature dependent absorption lengths show an analogous progression. Whereas PS also has an increasing curve, the PET curve demonstrates a constant decrease. This effect describes the experimental results that the thickness of PET sintering layers could not be increased by raising preheating temperature /1/. A quantitative determination above the melting point is not possible with the transmission method.

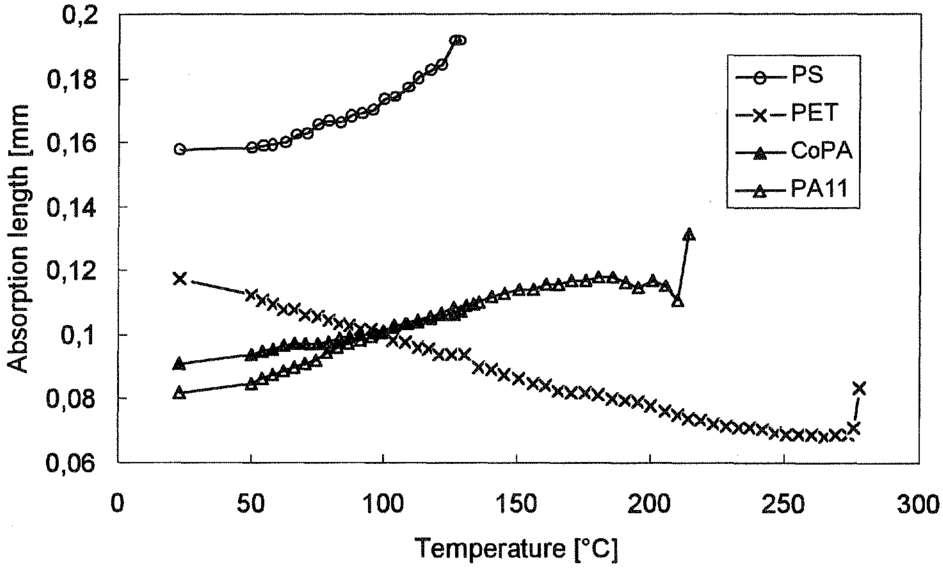


Fig. 2: Absorption length as function of temperature measured on 80µm films of the sintering materials PET, PS, PA 11 and CoPA

4 Laser process characteristics (SLS)

The main processing variables in the SLS application are the laser power, beam radius, scan speed, scan spacing, layer thickness as well as the temperature in the powder bed and process chamber.

The laser sintering lab device installed at IKP has a focused beam radius w_0=0.225mm. According to the scan spacing h_s, usually smaller than the laser beam radius, each laser intensity distribution (approximately Gaussian distribution) will partially overlay with the next one. Additionally, the polymer has less thermal conductivity in comparison with other materials. It is thus assumed that at the moment at which the laser is scanning and immediately afterwards it is likely that a heat block will arise on the surface of polymer powder. Hence, an overlapping variable γ to account this effect could be defined as follows /2/,

$$\gamma = \frac{I}{I_0} = 1 + 2 \cdot \sum_{i=1}^{N} \exp\left(\frac{-2 \cdot (i \cdot h_s)^2}{w_0^2}\right) \tag{3}$$

where h_s and w_0 are the scan spacing and the beam radius respectively.

The value for laser power, scan speed and scan spacing must be chosen appropriately, so as to best influence the properties of the sintered parts. For further investigation, the following assumptions are made :

1. The powder bed is treated as a homogenous and isotropic medium.
2. The heat transfer from the laser radiation to the material is a one dimensional case and the heat lost through the heat convection and radiation on the surface will be neglected.
3. The temperature dependent material properties will be approximated by an average value and the phase change and decomposition will be excluded.
4. The laser intensity and the scan speed are assumed constant, and also the average interaction time.
5. The cooling time between the superposition of the laser radiation with respect to a point on the plane can be neglected, since the thermal conductivity of polymer powder is relatively inferior (for v≥500 mm/s and average sample length of 50mm)

The equation to describe the heat transfer in the material caused by a Gaussian radiation distribution is shown in /3/. With consideration of the overlapping variable γ and the preheating temperature T_0, the modified equation is expressed as:

$$T(z,t) = \frac{AI_0\gamma}{\lambda}\left\{\begin{array}{l} 2\sqrt{\kappa t}\cdot \mathrm{ierfc}\left(\frac{z}{2\sqrt{\kappa t}}\right) - \frac{1}{a}\exp(-az) \\ + \frac{1}{2a}\exp(a^2\kappa t)\left[\exp(-az)\cdot \mathrm{erfc}\left(a\sqrt{\kappa t} - \frac{z}{2\sqrt{\kappa t}}\right) + \exp(az)\cdot \mathrm{erfc}\left(a\sqrt{\kappa t} + \frac{z}{2\sqrt{\kappa t}}\right)\right] \end{array}\right\} + T_0 \tag{4}$$

where A and a are the absorption quota and absorption coefficient respectively, when the material is subjected to a laser radiation.

5 Simplified heat transfer equations

The working curves are derived and utilized so as to ensure that the surface temperature should not exceed the decomposition temperature (*see A*), and so that there should simultaneously be sufficient laser power available for melting or sintering powder at a specific depth in the powder bed (*see B*).

A: Equation for $T \le T_z$ *on the surface of material, at* $z=0$

The temperature on the surface is easily to obtain by inserting $z=0$ into the equation (4) and it becomes

$$\frac{(T(0,t) - T_0)\cdot \lambda \cdot a}{A \cdot I_0} = \frac{2}{\sqrt{\pi}} a\sqrt{\kappa t} - \left[1 - \exp\left(a^2\kappa t\right)\cdot \mathrm{erfc}\left(a\sqrt{\kappa t}\right)\right] \tag{5}$$

The maximal temperature on the surface should not exceed the degradation temperature. The right side of the equation (5) could be further simplified, but the intermediate steps need not be shown in this work /4/. The simplified result delivers a clear relationship between the material properties and the relevant processing parameters:

$$\frac{(T(0,t)-T_0)\cdot\lambda}{A\cdot I_0}\approx a\cdot\kappa\cdot t \tag{6}$$

where the temperature difference $T(0,t)-T_0$ can be expressed as ΔT_{z0} instead and I_0 replaced by

$$I_0=\frac{2\cdot P}{\pi\cdot w_0{}^2}\,. \tag{7}$$

Hence, the maximal suitable laser power P_z which could be used in the process so that the material will not decompose is expressed as follows:

$$P_z=\frac{\pi\cdot v\cdot w_0\cdot\Delta T_{z0}\cdot c_p\cdot\rho}{4\cdot A\cdot a\cdot\gamma} \tag{8}$$

In addition this equation indicates the proportionality between absorption coefficient a and density ρ.

B: Equation for $T\geq T_m$ ***at a specific depth*** $z=z_m$

To guarantee a sufficient layer cohesion in the sintering parts, the layer thickness must usually be greater than 0.1 mm. This means that the temperature is supposed to reach the melting point at a specific desirable sintering depth in the powder bed $z=z_m$. Under this assumption, the terms in equation (4) can be reduced and the equation becomes:

$$T(z_m,t)-T_0=\frac{AI_0}{a\lambda}\cdot\exp(-az_m)\cdot\left[\exp\left(a^2\kappa t\right)-1\right] \tag{9}$$

where $T(z_m,t)-T_0$ can be replaced by the term ΔT_{m0} and I_0 likewise by equation (7). Thus, a minimal necessary laser power P_m to ensure a satisfactory sintering at the depth z_m is obtained.

$$P_m=\frac{\Delta T_{m0}\cdot\exp(a\cdot z_m)\cdot a\cdot\lambda\cdot\pi\cdot w_0{}^2}{2\cdot A\cdot\gamma}\cdot\left[\exp\left(a^2\cdot\kappa\cdot\frac{2w_0}{v}\right)-1\right]^{-1} \tag{10}$$

The calculations will be performed with average values (in this work not explicit described) of thermal properties detected accordingly DIN 53765 (DSC) and the thermogravimetric analysis (TGA). The thermal conductivity was estimated using the Zehner, Bauer and Schlünder equation (secondary parameters were taken into account) /5/.

The validity of the two simplified equations (8) and (10) will be verified at $z=0$ and $z=0.15$ mm respectively and illustrated in **Fig. 3**. As this reveals, the original and simplified equations coincide well with each other over the usual scan speed range, especially at $z=0.15$ mm. It is also useful to recognize that the interaction time has to lie in the range between 0.425 ms and 0.28 ms to fulfill the above mentioned requirements. A suitable working area related to the scan speed is then developed.

With CoPA, PA 11 and PS, it is quite easy to find an appropriate working area for a given layer thickness. In contrast to these three materials, PET seems less suitable for the laser sintering process because it is not possible to build a sufficient layer thickness without damaging the material on the surface. In addition to this, the absorption length decreases with the increasing temperature, which restricts the laser radiation around the surface region and the laser is thus not able to "penetrate" material to the required depth.

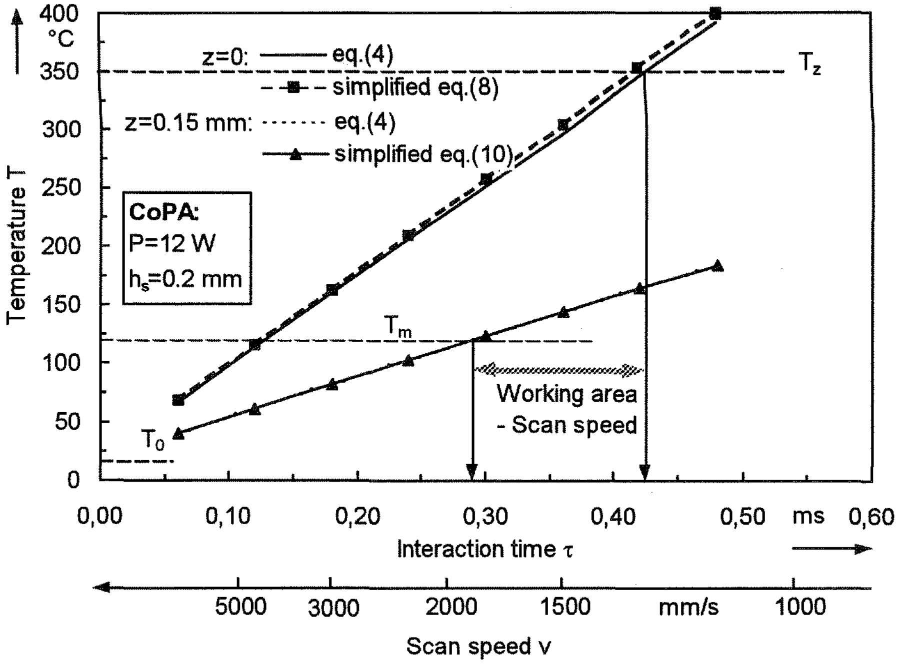


Fig.3: Comparison of the equation (4) and simplified ones

It is obvious that the P_z-line should lie above the P_m-line. The maximal possible sintering depth is to obtain through equating the equation (8) and (10) and it follows

$$z_m = \frac{1}{a}\cdot\ln\left[\frac{\Delta T_{z0}}{\Delta T_{m0}}\cdot\left(\frac{\exp(x)-1}{x}\right)\right] \quad \text{with } x = a^2\cdot\kappa\cdot\frac{2w_0}{v} \ll 1 \tag{11}$$

Because x is much smaller than 1 for the common polymer materials and processing conditions, the above equation could be further simplified to

$$z_m(T_0) = \frac{1}{a(T_0)}\cdot\ln\left(\frac{T_z - T_0}{T_m -. T_0}\right) \tag{12}$$

The progression of maximal achievable sintering depth with respect to the temperature dependent absorption length demonstrates consequently an asymptotic approach to the glass transition or melting temperature of the polymer respectively, see **Fig. 4**.

6 Comparison of calculated and measured sintering depths

To evaluate the validity of these equations, they could be directly compared with the experimental results. Through converting the equation (10), the achievable sintering depth could be expressed as a function of other material properties and processing parameters:

$$z_m = \frac{1}{a}\cdot\ln\left\{\frac{2\cdot A\cdot\gamma\cdot P_m}{\Delta T_{m0}\cdot a\cdot\lambda\cdot\pi\cdot w_0^{\,2}}\cdot\left[\exp\left(a^2\kappa\frac{2w_0}{v}\right)-1\right]\right\} \tag{13}$$

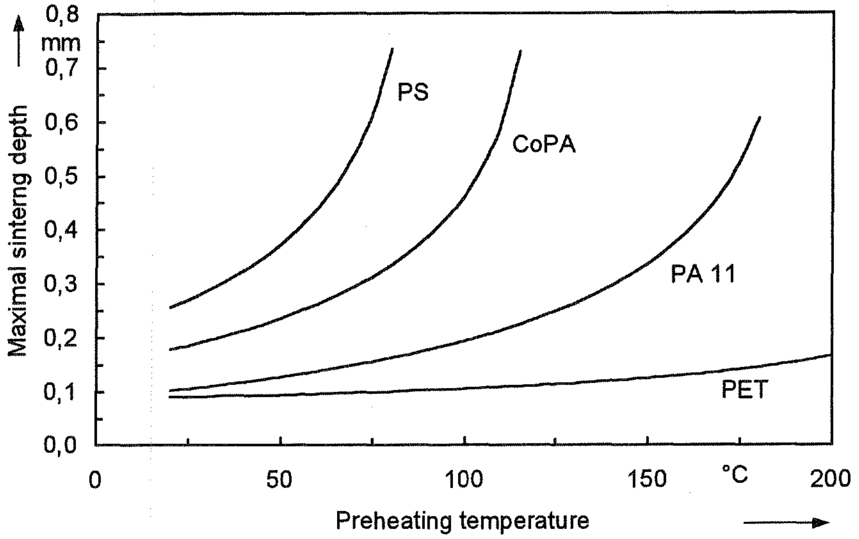
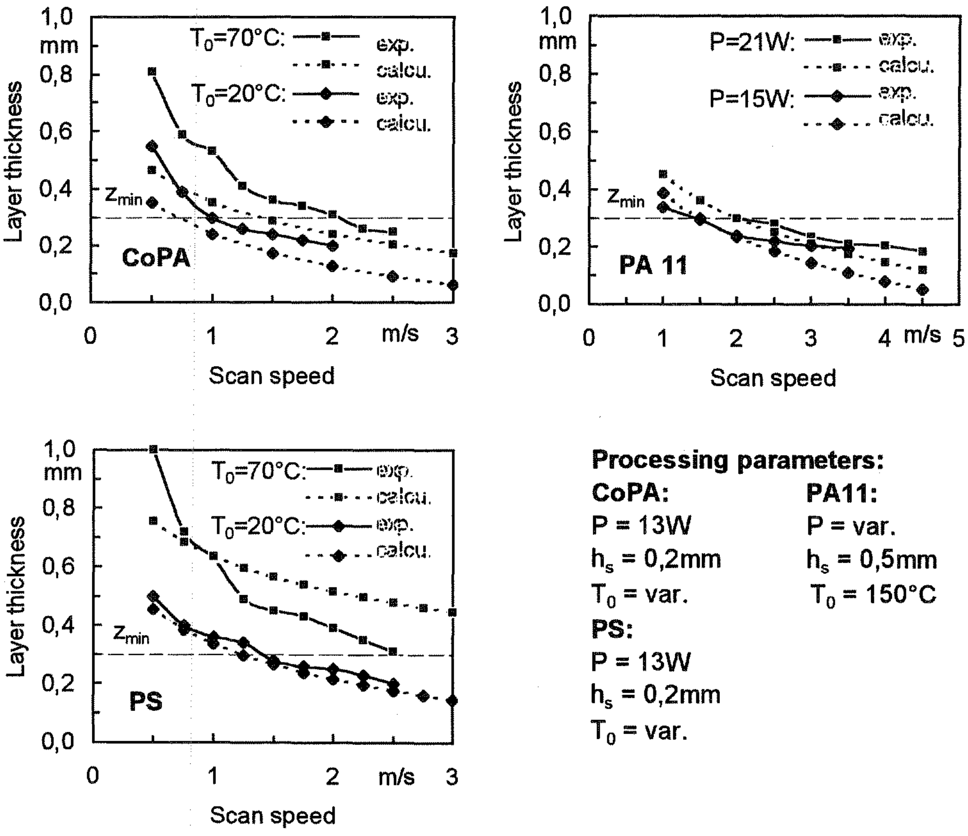


Fig. 4: Maximal reachable sintering depth for PS, CoPA, PA 11 and PET



Processing parameters:

CoPA:	**PA11:**
P = 13W	P = var.
h_s = 0,2mm	h_s = 0,5mm
T_0 = var.	T_0 = 150°C

PS:
P = 13W
h_s = 0,2mm
T_0 = var.

Fig. 5: Comparison of measured and calculated results in respect of sintering depth

It has to be stressed that the layer thickness was measured in experimental parts and this could differ from the sintering depth z_m in the theoretical view owing to the adhered particles on both sides of the sample. If the particle size is taken into consideration, through examination of the comparisons in **Fig. 5** it is clear that the experimental and calculated results show a very satisfactory agreement.

7 Conclusion and Outlook

By means of transmission IR-spectroscopy, a method for measuring temperature dependent absorption lengths of polymers, especially at a wavelength of 10.6µm (CO_2-Laser), is developed. This paper also points out simplified equations based on the one dimensional heat transfer equation with a volume heat source to set the processing parameters i.e. for the SLS process. The calculations show a satisfactory agreement with the measured results. The equations can be used to determine the working curves in the laser sintering technology and are suitable to estimate the processing parameters in other laser material processing as well such as, surface treatment, welding, cutting or drilling. The methodology of measuring the optical absorption length for CO_2-laser could be also extended to another wavelength range or laser types in the future.

8 Acknowledgement

The authors gratefully acknowledge the financial support of the German Research Foundation, DFG (Sfb 374), for this work. Thanks are due to Dr. Jialin Shen (Daimler-Benz AG) and Frieder Nagel (Fh-ICT), whose persistence and meticulousness contribute to the accomplishment of this work. The authors also appreciate the students for their considerable effort.

Nomenclature

A	Absorption quota [-]	T_m, T_z	Melting point and decomposition temperature [K]
a	Absorption coefficient [1/mm]	t	Interaction time [ms]
c	Relative concentration [-]	v	Scan speed [mm/s]
c_p	Specific heat capacity [J/g K]	w_0	Laser radius [mm]
d	IR-sample thickness [mm]	z	Depth in powder bed [mm]
E	Extinction [-]	ΔT_{m0}	Temperature difference of T_m and T_0
h_s	Scan spacing [mm]	ΔT_{z0}	Temperature difference of T_z and T_0
I_0, I	Entering and transmitting laser intensity [W/m^2]	γ	Defined overlapping variable [-]
l_a	Absorption length [mm]	ε	Extinction coefficient [mm]
P_m	Minimum necessary laser power [W]	κ	Thermal diffusivity [mm^2/s]
P_z	Maximum allowed laser power [W]	λ	Thermal conductivity [W/m K]
T_0	Preheating temperature [K]	ν	Frequency [cm^{-1}]
T_g	Glass temperature [K]		

Reference

1. Pfeifer, Rolf: Untersuchung thermoplastischer Werkstoffe für die Lasersinter-Technologie. Diplomarbeit, IKP, Universität Stuttgart (1997).
2. Su, Wie-Nien: Untersuchung des thermischen Verhaltens von Kunststoffen beim selektiven Lasersintern und Analyse der Prozessparameter. Diplomarbeit, IKP, Universität Stuttgart (1997).
3. Carslaw, H. S.; Jaeger, J. C.: Conduction of Heat in Solids. Oxford University Press (1959).
4. Keller, B.: Rapid Prototyping: Grundlagen zum selektiven Lasersintern von Polymerpulvern, Dissertation, Universität Stuttgart - to be published 1998.
5. Tsotsas, E.; Martin, H.: Thermal Conductivity of Packed Beds: A Review. Chem. Eng. Proc., Vol. 22, 19-37 (1987).