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MATERIAL MODELLING OF UV CURING POLYMERS FOR ADDITIVE MANUFACTURING PROCESSES

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Abstract. This contribution focuses on the experimental investigation and material modelling of the crosslinking of UV curing polymers used in additive manufacturing processes such as digital light processing and stereolithography. First photocalorimetric measurements with varying temperature and light intensity are shown. From the exothermic specific heat flows measured during the crosslinking reaction, the degree of cure can be determined for each experimental scenario. It is shown that the test temperature and light intensity have a significant influence on the crosslinking reaction.
A first modelling approach for the mathematical description of the crosslinking reaction is presented. Moreover, parameter identification of the proposed model is conducted using the commercial optimisation program LS-OPT®.

1 INTRODUCTION

Additive manufacturing (AM) is an innovative technology to create three dimensional objects with complex geometry. Although the technology has been used in industrial applications for decades, reliable and experimentally validated models for the design of printed components are still missing. Especially the material modelling and finite element analysis of UV curing polymers (so-called photopolymers) used in processes like digital light processing and stereolithography are challenging tasks. For this purpose, the crosslinking reaction in the additive manufacturing process must be described correctly by a phenomenological model and adapted to experimental data.
The crosslinking of photopolymers is initiated by the absorption of a light source. Besides that, the process depends strongly on the ambient temperature: a higher ambient temperature leads to faster crosslinking whereby the same applies to an increasing light intensity. Calorimetric measurements with the aid of an additional light source have proved useful for the experimental investigation of the crosslinking reaction of photopolymers [1].
Since the degree of cure directly influences the mechanical, thermal and chemical properties of

photopolymers, a validated material model for the degree of cure is essential for finite element analysis of additive manufacturing processes.

2 EXPERIMENTAL INVESTIGATION

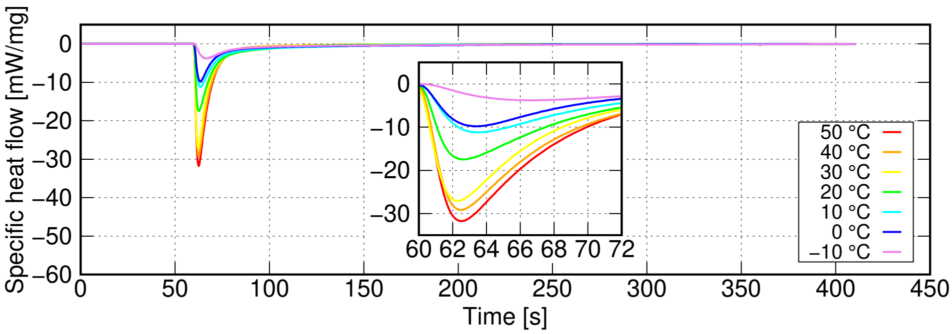
In order to understand and investigate the crosslinking process of commercial photopolymers used in additive manufacturing processes, differential photocalorimetry (DPC) measurements are conducted using the TA Instruments DSC Q2000 with an additional light source (OmniCure® S2000). The light source contains a high pressure 200 W mercury lamp with an spectral output of 320 to 500 nm.
To investigate the crosslinking reaction, the DSC measures the specific heat flow $\dot{h}$ between a sample in a pan and an empty reference pan during the crosslinking reaction. The following relationship is used to convert the specific heat flow into the degree of cure:

$$q(t) = \frac{\int_0^t \dot{h}(\tilde{t})\,\mathrm{d}\tilde{t}}{h_{\mathrm{tot}}} \tag{1}$$

Due to the normalisation to the maximum specific heat h_{tot} during the crosslinking reaction, the degree of cure assumes values between 0 and 1.
The commercial photopolymer LOCTITE® 3D 3830 was used for the photocalorimetric measurements. It is an acrylic compound for prototype development with low elongation at break, high tensile strength and low chemical shrinkage.
During the photocalorimetry measurement, following steps are performed subsequently for the determination of the specific heat flow $\dot{h}(\tilde{t})$ in eq. (1):

1. Equilibration of the measurement cell at a specific temperature (-10°C...50°C).
2. Isothermal phase of 60 s.
3. Irradiation of the specimen for 300 s at constant light intensity (5 mW/cm^2 and 10 mW/cm^2).
4. Isothermal phase of 60 s.

After finishing step four, the whole procedure is repeated with the cured specimen generating the baseline. The baseline is subtracted from the heat flow signal of the first measurement to consider only the heat flow of the crosslinking reaction. Otherwise, the light energy input would be taken into account.
In order to determine the maximum specific heat h_{tot} during the crosslinking reaction, an additional measurement at non-isothermal temperature is performed. During 300 s irradiation, the temperature is increased from 20 °C to 70 °C at 5 °C/min leading to a maximum specific heat of $h_{\mathrm{tot}} = 319.73$ J/g which is taken as reference value for the conversion of the specific heat during crosslinking reaction into degree of cure for all measurements.



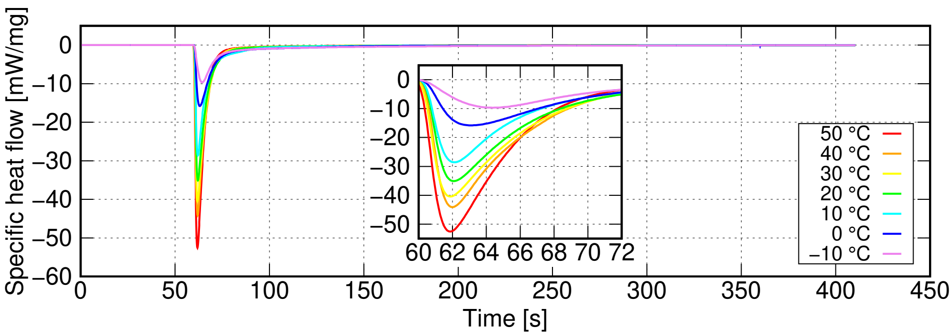


Figure 1: Measured specific heat flows after substraction of the baseline. Top: light intensity $I = 5$ mW/cm^2, bottom: light intensity $I = 10$ mW/cm^2.

The specific heat flows after substraction of the baseline of all measurements are shown in fig. 1. It can be clearly seen that the crosslinking reaction proceeds very quickly and that the specific heat flows have reached their maximum value after only a few seconds. Additionally, it is obvious that a higher light intensity leads to higher maximum values in the heat flows and that a higher temperature accelerates the reaction.
Moreover, complete curing is not achieved at low temperatures and light intensities and the crosslinking reaction is stopped prematurely, cf. fig. 2. The maximum attainable degrees of cure q_{max} for all measurements are listed in table 1. It can be seen that an almost fully cured material is achieved at a temperature of 50 °C, regardless of the light intensity. This result must definitely be taken into account when formulating the material model for the degree of cure.

Table 1: Maximum attainable degree of cure q_{max} of all measurements

	−10 °C	0 °C	10 °C	20 °C	30 °C	40 °C	50 °C
5 mW/cm^2	0.469	0.619	0.675	0.775	0.851	0.904	0.947
10 mW/cm^2	0.593	0.685	0.775	0.845	0.907	0.949	0.997

3 MATERIAL MODELLING

The differential equation for the degree of cure q depends on time, light intensity $I(z(t),t)$ and temperature T. Following the work of Kamal [2], an autocatalytic model of $(m+n)$th order incorporating the maximum attainable degree of cure $q_{\max}$ is applied for the degree of cure q:

$$\dot{q} = \left(k_1\left(I\left(z\left(t\right),t\right),T\right) + k_2\left(I\left(z\left(t\right),t\right),T\right)q^m\right)\left(q_{\max} - q\right)^n \ . \tag{2}$$

Here, $I\left(z\left(t\right),t\right)$ denotes the time- and location-dependent light intensity. The light intensity must depend on the vertical location $z\left(t\right)$ since it evolves during the printing process. The maximum attainable degree of cure acts as a limit value. The constants

$$k_i\left(I\left(z\left(t\right),t\right),T\right) = k_{0i}\left(T\right) I^b\left(z\left(t\right),t\right) \tag{3}$$

with the Arrhenius type equations

$$k_{0i}\left(T\right) = A_i \exp\left(-\frac{E_i}{RT}\right) \tag{4}$$

are based on the proposal by Maffezzoli and Terzi [3] depending on light intensity $I\left(z\left(t\right),t\right)$ and temperature T. If no light source is present, i.e. $I\left(z\left(t\right),t\right) = 0$, the crosslinking reaction is stopped. A_i and E_i are pre-exponential factors and activation energies, respectively. R denotes the universal gas constant. The additional parameter b is introduced for a better representation of experimental data.

4 PARAMETER IDENTIFICATION AND VALIDATION

The parameters in eq. (2) are identified using the commerical optimisation program LS-OPT® in combination with MATLAB®'s `ode45` solver. LS-OPT® uses the sequential response surface method for optimisation. For further informations see [4].

The parameter identification depends strongly on the initial values. The parameters listed in table 2 represent the first result of the parameter identification which identified the equation for the degree of cure on the measurement results. For simplification, the particular maximum attainable degree of cure was specified as a parameter in order to achieve a better agreement with the measurement results.

Fig. 2 shows the simulations of the degree of cure compared to all measurements according to eqs. (1) and (2) with identified model parameters.

Table 2: Identified model parameters for the description of the crosslinking reaction

A_1	A_2	E_1	E_2	R	m	n	b
$\left(\mathrm{cm}^2\right)^b/\left(\left(\mathrm{mW}\right)^b\mathrm{s}\right)$	$\left(\mathrm{cm}^2\right)^b/\left(\left(\mathrm{mW}\right)^b\mathrm{s}\right)$	J/mol	J/mol	J/(mol K)	-	-	-
0.2	0.6	9744	6000	8.314	6	2.377	1.901

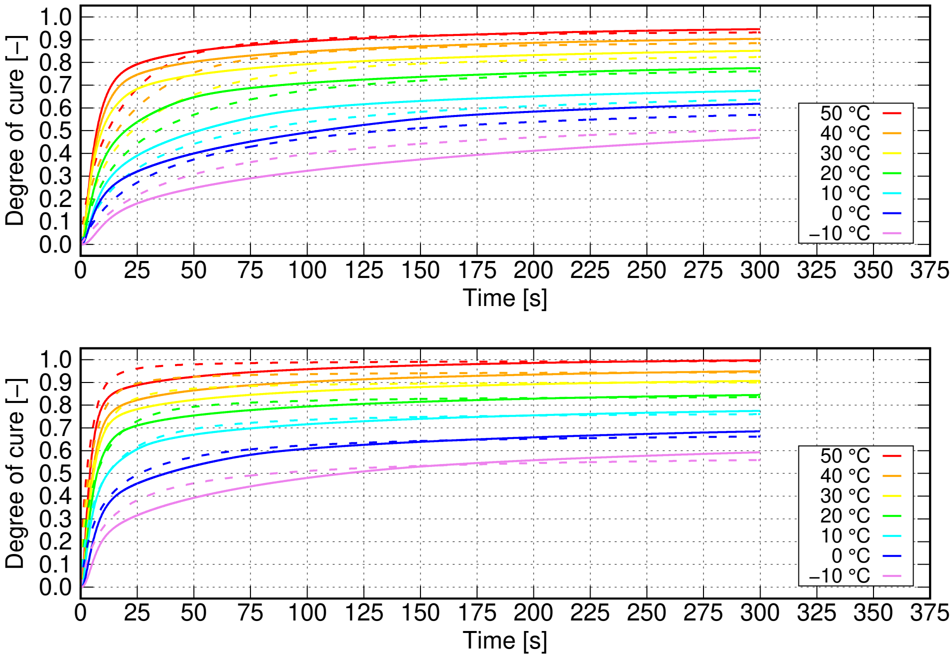


Figure 2: Measurement (—) and simulation (- -) of the degree of cure q according to eqs. (1) and (2) with identified model parameters. Top: light intensity $I = 5$ mW/cm^2, bottom: light intensity $I = 10$ mW/cm^2.

The simulations show a good agreement with the measurement results, although the maximum attainable degree of cure has been specified as a parameter. Especially the temperature dependence and the rapid increase of the degree of cure within the first seconds of irradiation are well represented.

5 SUMMARY AND OUTLOOK

First measurements for the experimental characterisation of the crosslinking reaction of photopolymers used in additive manufacturing processes are presented in this contribution. It is shown that temperature and light intensity have a significant influence on the crosslinking reaction.

A differential equation incorporating the maximum attainable degree of cure q_{max} is proposed for the phenomenological description of the degree of cure. Parameter identification using commercial optimisation tools is carried out. The validation shows a good agreement between measurements and simulations.

Forthcoming considerations include the correct description of the maximum attainable degree of cure as a function of temperature and light intensity:

$$q_{\text{max}} = f\,(T, I) \tag{5}$$

Kolmeder et al., for example, have already carried out work for this purpose [5].

6 ACKNOWLEDGEMENT

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REFERENCES

[1] Höhne, G.W.H., Hemminger, W.F. and Flammersheim, H.-J. *Differential scanning calorimetry*. Springer-Verlag Berlin Heidelberg, (2003).

[2] Kamal, M.R. Thermoset Characterization for Moldability Analysis. *Polymer Engineering and Science* (1974) **14**:231–239.

[3] Maffezzoli, A. and Terzi, R. Effect of irraditation intensity on the isothermal photopolymerization kinetics of acrylic resins for stereolithography. *Thermochimica Acta* (1998) **321**:111–121.

[4] Stander, N., Roux, W., Basudhar, A., Eggleston, T., Goel, T. and Craig, K. *LS-OPT®* *User's Manual*. Livermore Software Technology Corporation, (2015).

[5] Kolmeder, S., Lion, A., Landgrad, R. and Ihlemann, J. Thermophysical properties and material modelling of acrylic bone cements used in vertebroplasty. *J Therm Anal Calorim* (2011) **105**:705–718.