

ERGEBNISSE AUS DER PRODUKTIONSTECHNIK

Emely Marie Harnisch

Two-Photon Polymerization on Metal Surfaces for Structuring Moulding Tools



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Zwei-Photonen-Polymerisation auf metallischen Oberflächen zur Strukturierung von Formeinsätzen

Von der Fakultät für Maschinenwesen
der Rheinisch-Westfälischen Technischen Hochschule Aachen
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*Für Eveline, Markus
sowie
Edelgard & Paul*

*"One child, one teacher, one book and one pen can change the world"
- Malala Yousafzai*

Vorwort

Diese Dissertation entstand während meiner Tätigkeit als wissenschaftliche Mitarbeiterin am Fraunhofer-Institut für Produktionstechnologie IPT in der Abteilung Produktionsmesstechnik. An dieser Stelle möchte ich einigen Personen danken, die es mir ermöglichen, diese Arbeit anzufertigen und die mich bei diesem Vorhaben unterstützen.

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Summary

Given the fact of the increasing meaning of individual and functional micro- or nano-structures, it is of high interest to open up two-photon polymerization (TPP) as a structuring technology for production. TPP offers real 3D capability while providing a line width beyond the diffraction limit, so arbitrary geometries with e. g. optical, photonic or biological functionalities can be realized. The disadvantage about this technology is its relative small throughput when comparing it with established process chains in production, so the aim is to open up TPP as a mastering technology for metal substrates that serve as tools for injection moulding.

Within this thesis, the main research question, if TPP is suitable for the structuring of metal tools for injection moulding, is addressed. To control the process and allow for a prediction of the voxel shape on metal surfaces, a comprehensive model is implemented in Matlab considering the temperature development in the metal surface during TPP, the polymerization process in the photosensitive hybrid polymer OrmoComp® as well as the final intensity distribution resulting in a stationary wave due to the superposition of incident and reflected laser beams. OrmoComp® is regarded here, since it is a so called hybrid polymer, containing SiO_2 -groups, that cause the polymerized material to be more resistant against the harsh conditions during injection moulding like high pressures and temperatures.

By discretizing the heat conduction equation, the temperatures in three different materials, that are established as substrates for injection moulding, are calculated during TPP. To gain exact information about the polymerization process, the reaction equations for OrmoComp® are set up, while the corresponding transition states are simulated in Mopac to calculate the reaction constants. Using the model developed by Nitin Uppal and the reaction constants, the temperature, the monomer concentration, radical concentration, inhibitor concentration and photo initiator concentration are calculated via five coupled differential equations. By deriving the monomer conversion, the final voxel size can be predicted with this model, allowing for a comparison between the voxel size with regard to intensity distribution and the voxel size caused by polymerization. Within a third model, the final intensity distribution during TPP on metal surfaces is calculated by superposing the incident and reflected focussed laser beam. By using a threshold value in dependence on the results of the polymerization calculation, the extent of the polymerized area is computed.

To verify the results of the model, ascending scans consisting of simple lines on the three substrate materials, each with three different surface roughnesses were performed. A comparison of the line's cross sections from the experiments and the calculated voxel shape shows good agreement, also when considering variations of the parameters like the exposure dose. Thus, a model was implemented, that allows for the prediction of the resulting voxel shape during TPP on metal surfaces. Finally, simple geometries like cubes and semispheres were written on steel and casted with injection moulding for a validation.

Zusammenfassung

Vor dem Hintergrund der zunehmenden Bedeutung individueller und funktionaler Mikro- und Nanostrukturen ist es von großem Interesse, das Verfahren der Zwei-Photonen-Polymerisation (ZPP) für die Produktion zu erschließen. Die ZPP erlaubt volle 3D-Fähigkeit bei gleichzeitiger Linienbreite unterhalb des Beugungslimits, so dass beliebige Geometrien mit bspw. optischer, photonischer oder biologischer Funktionalität realisierbar sind. Im Vergleich zu etablierten Prozessketten ist der Durchsatz der ZPP gering, so dass das Ziel am Fraunhofer-Institut für Produktionstechnologie IPT darin besteht, das Verfahren als Masteringtechnologie für metallische Substrate zu erschließen, welche dann als strukturierte Formeinsätze im Spritzguss verwendet werden.

Im Rahmen dieser Arbeit wird die Hauptforschungsfrage, ob die ZPP zur Strukturierung von metallischen Werkzeugen für den Spritzguss geeignet ist, adressiert. Um den Prozess zu beherrschen und die Voxelausprägung auf Metall vorherzusagen, wird ein umfangreiches Modell in Matlab implementiert. Dieses berücksichtigt die Temperaturrentwicklung während der ZPP im Substrat, den Polymerisationsprozess in dem photosensitiven Hybridpolymer OrmoComp® sowie die resultierende Intensitätsverteilung, die aufgrund der Überlagerung von einfallendem und reflektiertem Laserstrahl einer stehenden Welle entspricht. Als Photopolymer wurde das Hybridmaterial OrmoComp® ausgewählt, da es aufgrund der enthaltenen SiO_2 -Gruppen im polymerisierten Zustand eine ausreichende Stabilität gegenüber hohen Temperaturen und Drücken aufweist.

Die Berechnung der Temperatur im Substrat während der ZPP erfolgt durch die Diskretisierung der Wärmeleitungsgleichung, wobei drei Substratmaterialien angenommen wurden, die im Spritzguss etabliert sind. Um den Polymerisationsprozess zu simulieren, wurden die Reaktionsgleichungen von OrmoComp® aufgestellt und die jeweiligen Übergangszustände im Mopac ermittelt, was die Berechnung der Reaktionskonstanten erlaubt. Mittels dieser berechneten Reaktionskonstanten und des Modells von Nitin Uppal, ist eine Darstellung der Temperatur sowie der Konzentrationen der Polymerbestandteile möglich, was eine Aussage über die Voxelgröße erlaubt. Der dritte Teil des Modells betrachtet die Intensitätsverteilung während der ZPP auf metallischen Oberflächen durch Überlagerung des einfallenden und reflektierten fokussierten Laserstrahls. Das Ausmaß der Polymerisation wird durch einen Schwellwert berücksichtigt, was schließlich die Darstellung der finalen Voxelform ermöglicht.

Zur Verifizierung der Simulationsergebnisse wurde zudem ein ascending scan aus einfachen Linien auf den drei betrachteten Substratmaterialien, je mit drei verschiedenen Rauheiten, durchgeführt. Dabei zeigen die experimentellen Linienquerschnitte und die berechneten Voxel auch unter Berücksichtigung verschiedener Parametervariationen eine gute Übereinstimmung. Die Entformbarkeit einfacher, auf Stahl hergestellter Geometrien mittels Spritzguss wird in einer Validierung bewiesen.

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Nomenclature

Abbreviations

μTM	Microtransfer moulding
2PII	Two-color photo-initiation/inhibition
AFM	Atomic force microscope
AG	Aktiengesellschaft
AM 1	Austin model 1
BHT	2,6-Di-tert-butyl-4-methylphenol
BMBF	Bundesministerium für Bildung und Forschung
CGH	Computer generated hologram
CM	Confocal microscope
CML	Chemical markup language
CNDO	Complete neglect of differential overlap
COSMO	conductor-like screening model
CPU	Central processing unit
DEQ	Differential equation
DFT	Density Functional Theory
DL-SPPW	Dielectric loaded surface-plasmon-polariton waveguides
DMD	Digital multimirror device
DOE	Diffractive optical element
FDM	Finite difference method
FDTD	Finite difference time domain
FI	Find interface
FIB	Focussed ion beam
FORTH	Foundation for Research and Technology
FOV	Field of view
FT	Fourier transformation
FTCS	Forward-time centered-space
FVM	Finite volume method
FWHM	Full width at half maximum
GGA	Generalized gradient approximation

GmbH	Gesellschaft mit beschränkter Haftung
GT	Galvoscaner Technology
GTO	Gaussian-type orbitals
HCE	Heat conduction equation
HF	Hartree Fock
HMO	Hückel molecular orbital
HoF	Heat of formation
IPT	Institute for Production Technology
IRG	2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1s
KMU	Kleine und mittelständische Unternehmen
LCAO	Linear combination of atomic orbitals
LDA	Local density approximation
LED	Light Emitting Diode
LIFT	Laser-induced forward transfer
MA- μ TM	Membrane assisted microtransfer moulding
MEMS	Microelectromechanical systems
MNDO	Modified neglect of differential overlap
MO	Molecular orbital
MOEMS	microoptoelectromechanical systems
MRT	micro resist technology GmbH
MSDS	Material safety data sheet
NA	Numerical aperture
NDDO	Neglect of diatomic differential overlap
NDO	Neglect of differential overlap
NIL	Nano imprint lithography
NMM	Nano measuring machine
OLED	Organic Light Emitting Diode
OPA	One-photon absorption
PDMS	Polydimethyl siloxane
PES	Potential energy surface
PETPP	Plasmonic resonance enhanced two-photon polymerization
PM	Parameterized model
PMMA	Polymethylmethacrylate
PSF	Point spread function
RAPID	Resolution augmentation through photo-induced deactivation
RHF	Restricted Hartree Fock
SEM	Scanning electron microscope
SFB	Sonderforschungsbereich
SLM	Spatial light modulator

SME	Small and medium enterprises
SPECTARIS ...	Verband der Hightech-Industrie
SPP	Surface plasmon polaritons
STED	Stimulated-emission-depletion
STO	Slater-type orbitals
TE	Transverse electric
TH	Threshold
THIO	thioxanthen-9-one
TM	Transverse magnetic
TPA	Two-photon absorption
TPL	Two-photon lithography
TPO	Diphenyl(2,4,6-trimethylbenzoyl)phosphinoxid
TPP	Two-photon polymerization
TR	Transregio
TS	Transition state
UFF	Universal force field
UG	Unternehmergegesellschaft
UHF	Unrestricted Hartree Fock
UV	Ultra violet
VDMA	Verband Deutscher Maschinen- und Anlagenbau
WLI	White light interferometry
ZDO	Zero differential overlap
ZPE	Zero-point energy
ZVEI	Zentralverband Elektrotechnik- und Elektronikindustrie

Symbols

\AA	Angstrom
α	Molar absorption coefficient
\mathbf{g}	Gradient matrix, 2.4.5
\mathbf{H}	Hessian matrix, 2.4.5
χ_i	Atomic orbitals
δ	Phase shift
δ	TPA cross section of photoinitiator, 4.2.4
$\Delta_{\neq}G_m^{\circ}$	Gibbs energy of activation
$\Delta_{\neq}H_m^{\circ}$	Enthalpy of activation
$\Delta_{\neq}S_m^{\circ}$	Entropy of activation
\dot{Q}	Heat flux
ϵ_a	Orbital energies

ϵ_i	Energy state in Boltzmann distribution
ϵ_r	Relative dielectric constant
\hat{H}	Hamiltonian operator
\hat{n}	Complex refractive index
\hbar	$\hbar = \frac{h}{2\pi}$
κ	Attenuation, 2.2
κ	Temperature conductivity, 2.3.2
κ	Transmission coefficient of the transition state, 2.4.4
λ	Thermal conductivity, 4.1
$[M]$	Concentration of monomer
$[P]$	Concentration of photoinitiator
$[R]$	Concentration of radical
$[Z]$	Concentration of inhibitor
$\langle v_{rel} \rangle$	Medium relative velocity
μ	Magnetic permeability in matter
μ	Reduced mass of molecules, 2.4.4
μ_0	Magnetic permeability in vacuum
μ_r	Relative magnetic permeability
Φ	Photon flux
ψ	Wave function
ρ	Mass density
σ_2	TPA cross section
σ_{AB}	Collision cross section
\mathbf{B}	Magnetic flux density
\mathbf{H}	Magnetic field strength
\mathbf{q}	Heat flux density
\mathbf{S}	Poynting vector
θ_j	Basis functions
φ	Phase
\vec{E}	Electric field strength, 4.3
\vec{H}	Magnetic field strength, 4.3
\vec{S}	Poynting vector, 4.3
A	Helmholtz energy, 2.4.3
A	Preexponential factor
A	Surface, 4.1
C	Heat capacity
c	Molar concentration, 2.4.4
c	Specific heat capacity, 2.3.2
c°	Standard concentration

c_p	Specific heat capacity
c_0	Speed of light in vacuum
d	Diameter of a molecule, 2.4.4
d	Molecular diffusion, 4.2.4
E	Energy
e	Charge of an electron
E_a	Activation energy, 2.4.3
E_{SCF}	Standard enthalpy of formation at 298 K
F	Farad, A.2.1
f	Frequency
f_1	Fock operator
G	Gibbs energy
H	Enthalpy
h	Planck's constant
H_m^Θ	Standard enthalpy
h_1	Core hamiltonian
H_f	Standard enthalpy of formation, 4.2.3
H_T	Correction of enthalpy due to temperature change
J	Coulomb operator
K	Exchange operator, 2.4.2
K	Heat conductivity, 2.3.2
k	Rate constant of a chemical reaction
k^\neq	Rate constant for the decay of the activated complex into products
k_B	Boltzmann constant
K_c^\neq	Equilibrium constant for the equilibrium between the reactants and the transition state
k_p	Reaction constant propagation
k_t	Reaction constant termination
k_Z	Reaction constant inhibition
m	Mass
m	Meter, A.2.1
N	Total number of molecules
n	Real part of complex refractive index
N_A	Avogadro constant
n_i	Number of molecules in energy state ϵ_i
P	Laser power
P	Steric factor for calculations concerning reaction kinetics
p	Pressure
$P_{e,i}$	Peclet number, 4.1
q	Heat

Q_L	Heat source
R	Gas constant
r	Complex reflection coefficient
r	Radius
$R(z)$	Radius of curvature of wave fronts
S	Entropy
S	Overlap integral
T	Period of time
T	Temperature
t	Complex transmission coefficient
U	Internal energy
V	Potential energy
V	Visibility, 2.2.3
V	Volume
v	Velocity
w	Work
$w(z)$	Beam radius depending on z
w_0	Beam waist
Z	Number of collisions per time and volume element
z'	Partition function
q_0	Target geometry
q_i	Initial geometry
z_R	Rayleigh length

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