Multiphysics modelling of photo-polymerization in DLP printing process and validation

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Materials Solutions, TNO
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Brightlands Materials Center

- **Public-private partnership** initiative founded March 19, 2015 by TNO and the Province of Limburg.
- Focusing on **sustainable** innovations in **polymers**.
- Three programs driven by **application challenges**, together with universities and industry partners.
Additive Manufacturing Program – Focus

Multi-material photopolymer for new (responsive) functionalities

polymers with continuous fibers for reinforcement and sensing
Materials Challenges

- Quality: warpage and residual stress, ...
- Stability: structural performance at high temperature and long term behavior, ...
- Multi-material, 4D printing and etc.

Warpage in products
Objective

To use *modeling and simulation* in order to link *materials* and *process* for further control in *SLA/DLP printing*

- Models are needed to understand and improve:
  - *Process conditions* to meet or contribute to the object specifications
  - *Material compositions* to meet or contribute to the object specifications
Photo-polymerization in SLA/DLP

- SLA: Stereolithography Apparatus; DLP: Digital Light Printing
- The photo-polymerization is the core of SLA/DLP technology.

The double-bond conversion can be used to present the reaction.
Multiphysics Modelling

Kinetic
1 -> R
Propagation
Termination

Thermal

Material properties + shrinkage

Mechanical

\( \frac{\partial [M]}{\partial t} = -A[M]\sqrt{t} \)
M.D. Goodner and C.N. Bowman, 2002

Heat Transfer in Solids (ht)
- Domains
  - Solid 1
  - Initial Values 1
  - Heat Transfer in Solids - Material
  - Heat Source - Light
  - Heat Source - Reaction

Solid Mechanics (solid)
- Domains
  - Linear Elastic Material 1
  - Initial Values 1
  - Linear Elastic Material - Material

Photopolymerization, no diffusion (dode)
- Domains
  - Distributed ODE 1
  - Initial Values 1

Beer-Lamber Law (cdeq)
- Domains
  - Convection-Diffusion Equation 1
  - Initial Values 1

Multiphysics
- Thermal Expansion 1 (te1)
- Temperature Coupling 1 (tc1)
- Thermal Expansion 2 (te2)
Material Characterization

- Parameters of the kinetics model are obtained based on the experiments.

### Material Contents

<table>
<thead>
<tr>
<th>Property</th>
<th>Variable</th>
<th>Value</th>
<th>Unit</th>
<th>Property group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>rho</td>
<td>rho_t</td>
<td>kg/m³</td>
<td>Basic</td>
</tr>
<tr>
<td>Heat capacity at constant pressure</td>
<td>Cp</td>
<td>Cp_t</td>
<td>J/(kg·K)</td>
<td>Basic</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>k_iso ; k_i ; k_t</td>
<td></td>
<td>W/(m·K)</td>
<td>Basic</td>
</tr>
<tr>
<td>Coefficient of thermal expansion</td>
<td>alpha_is ; alpha_t</td>
<td></td>
<td>1/K</td>
<td>Basic</td>
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<tr>
<td>Bulk modulus</td>
<td>K</td>
<td>K_m_t</td>
<td>N/m²</td>
<td>Bulk modulus and shear moduli</td>
</tr>
<tr>
<td>Shear modulus</td>
<td>G</td>
<td>G_m_t</td>
<td>N/m²</td>
<td>Bulk modulus and shear moduli</td>
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<td>Poisson’s ratio</td>
<td>nu</td>
<td>nu_t</td>
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<tr>
<td>Young’s modulus</td>
<td>E</td>
<td>E_m_t</td>
<td>Pa</td>
<td>Basic</td>
</tr>
</tbody>
</table>

In-situ FTIR

![Conversion vs. time graph](conversion_graph.png)

Rheometer

![Rheometer and shear modulus graph](rheometer_graph.png)
Experimental Validation

Adjust the exposure time of the last layer.
Conclusions and Outlook

- With COMSOL, a Multiphysics model was developed to investigate effects of **process conditions** and **material compositions** on **deformation** and **residual stress** of a **multi-layered DLP-printed** product.
- Required parameters can be obtained based on commercial-available experimental set-up. It gives a possibility for **standardization**.
- Validation showed a **good agreement** if a non-linear material model (plasticity) was adopted.
- We are
  - improving process conditions and new designs based on the developed model.
  - improving the accuracy and the computational cost of the model.
  - applying this model to other photo-polymers.
  - ...
Thank you for your attention!