Applied R&D Projects in Additive Manufacturing

Hélio Jorge
CTCV-Technology Centre for Ceramics and Glass. Coimbra. Portugal

10-09-2019. 7th Shaping Conference. Aveiro. Portugal
• CTCV introduction
• Overview of the AM technologies for ceramics in the market
• An R&D collaborative project of robocasting for decorative ware
• A study on the processing of alumina by robocasting
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CTCV Introduction

• Established in 1987 by ceramic and glass industrial associations and companies
• Non-profit organisation
• One of the Centres of Technology Interface (CIT) of Portugal
• Located in Coimbra, Centro Region, Portugal
• Business Activities
  • Innovation and Development (R&D)
  • Technical Consultancy
  • Testing
  • Training
CTCV Introduction

- 60 collaborators | 550 costumers (2018)
- Accredited organisation for supply of services under Portuguese financial instruments - Innovation/R&D, Entrepreneurship, Incubation, Industry 4.0 e and Circular Economy
- Participation in more than 20 R&D projects (H2020, Portugal 2020 and others)
- Member of Portuguese clusters: PRODUTECH, Sustainable Habitat Cluster and MOBINOV
Mission of the R&D Department

- Industrial research, development and innovation (R&Di)
  TRL starting from Level 3
- Innovation, Intellectual Property and Technology Transfer
- Participation in R&D and innovation funded projects
Infrastructure
R&D Department

Activities

• Applied research and development
• Pre-industrial studies
• Prototyping
• Small production

Technical Fields

• Materials
• Ceramics
• Manufacturing technologies
• Digital technologies for product development
Technical fields

**MATERIALS**
- ceramic material
  - traditional ceramics
  - technical and advanced ceramics
- integration with other material families
  - polymers
  - nanomaterials

**MANUFACTURING TECHNOLOGIES**
- ceramic technologies
  - pressing
  - extrusion
  - sintering / firing
- powder technologies
  - powder injection moulding
    - ceramic injection moulding
    - metal injection moulding
  - additive manufacturing
    - robocasting
    - fused filament fabrication

**PRODUCT DEVELOPMENT**
- reverse engineering
- virtual modelling, photo reality
- rapid prototyping
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AM methods for ceramics available in market

Classification of the methods for additive manufacturing:

- Photopolimerisation
- Material injection
- Material extrusion
- Lamination
- Binder jetting
- Powder melting
- Direct deposition

- Liquids
- Solids
- Powders

3D Printing ➔ Drying / Debinding ➔ Firing / Sintering
Photopolymerisation / Stereolithography / SLA

**Materials (Suspension)**
- Alumina, Zirconia, Silicon nitride
- Tricalcium Phosphate TCP and hydroxyapatite
- density: >99%

**Potential applications**
- Biomedicine / bone replacement
- Dental restoration
- Casting cores
- Technical ceramics apps

**Available technologies**
- Lithoz (Austria)
- 3D Ceram (France)
- Admatec (Holand)
Casting tool
Silica
Decorative piece glazed alumina-silica

Materials (Powder)

- Gypsum / Binder
- Alumina - Silica
- Silica
- density: ~50%

Potential applications

- Casting tools
- Refractory
- Glazed decorative ware

Available technologies

- 3DSystems (USA)
- Voxeljet (Germany)
- Tethon3D (USA)
Material extrusion

Materials (Paste)

- Plastic clay
- ...

Available technologies

- WASP (Italy)
- Lutum (Holand)
- 3D Potter (USA)
- Stone Flower (Germany)

Potential applications

- Decorative ware
- Sanitary ware
- Ceramic craft
- ...

Decorative pieces (green state)
Porcelain (CTCV)
CTCV introduction

Overview of the AM technologies for ceramics in the market

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RoboCer.3D Project

Porcelanas da Costa Verde (Porcelain table ware manufacturer)
University of Aveiro
CTCV-Technology Centre for Ceramics and Glass
Additive manufacturing of porcelain ware

**Used technology:** Robocasting (or LDM - liquid dispensing modelling)

**Technology developments:**

- Ceramic body composition manipulation
- Printer programming using a slicing software
- Setting up of the printing process
- Glazing and firing testing
- Printing validation tests:
  - Conventional geometry parts
  - Design-for-3DP new parts
Printing of a decorative piece of 10x10x40cm

1st step: Evaluation of the print ability of the part

Original model

Reviewed model
2nd step: Slicing / Print programming

<table>
<thead>
<tr>
<th><strong>Cura Parameter</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Nozzle size</td>
<td>0,8 mm</td>
</tr>
<tr>
<td>Layer thickness</td>
<td>0,7 mm</td>
</tr>
<tr>
<td>Printing speed</td>
<td>50 mm/s</td>
</tr>
<tr>
<td>Wall thickness</td>
<td>3,2 mm [4 contornos]</td>
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<tr>
<td>Bottom/Top thickness</td>
<td>4 mm</td>
</tr>
<tr>
<td>Fill density</td>
<td>0%</td>
</tr>
</tbody>
</table>
Printing of a decorative piece of 10x10x40cm

3th step: Printing
3th step: Printing

Printing of a decorative piece of 10x10x40cm
Printing of a decorative piece of 10x10x40cm

Glazed part
Examples of parts produced by Robocasting

Green parts

Glazed parts

Fired parts
Technological parameters

Sintering shrinkage: effect of building orientation (ZZ vs XY)

- Shrinkage in ZZ higher than in XY
  - ZZ: 16-22%
  - XY: 9-11%
Technological parameters

Densification and mechanical strength: comparasion with extrusion process and the influence of building direction

<table>
<thead>
<tr>
<th></th>
<th>Robocasting Printed in H position</th>
<th>Robocasting Printed in V position</th>
<th>Extrusion Printed in H position</th>
<th>Extrusion Printed in V position</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water absorption (wt%)</td>
<td>0.14 ± 0.07</td>
<td>0.25 ± 0.05</td>
<td>0.16 ± 0.04</td>
<td></td>
</tr>
<tr>
<td>Apparent density (g/cm³)</td>
<td>2.38 ± 0.01</td>
<td>2.36 ± 0.01</td>
<td>2.38 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>Flexure strength (MPa)</td>
<td>58 ± 13</td>
<td>69 ± 10</td>
<td>71 ± 5</td>
<td></td>
</tr>
</tbody>
</table>

- Low variation in WA and density
- Difference of 15% in FS between the material printed in 2 positions
- Resistência do material impresso na posição V similar à referência
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Processing of alumina suspensions by robocasting

MSc Thesis of Filipa Lopes
Supervised by Prof. Luísa Durães* and Hélio Jorge**

* CIEPQPF. Department of Chemical Engineering. University of Coimbra. Portugal
** CTCV-Technology Centre for Ceramics and Glass. Coimbra. Portugal
Robocasting system used

- **Photopolimerization based methods**
  - high final shape precision
  - small size parts
  - high densification materials
  - but available at a high investment cost

- **Robocasting / LDM**
  - medium shape precision or pre-forms
  - higher size parts
  - Expected to accessed with low/medium investment cost
Robocasting system used

Pasta

V
Q
P
Q
P_{cl}
7 \text{ bar}

W
Phase 1 - Assessment of the print ability of ceramic formulations

MATERIALS

- Alumina 99.8%, D50 = 0.4 μm [Almatis CT 3000 SG]

- 2 formulation systems:
  - Sacarose, Polyvinyl alcohol (PVA), Oleic acid (OA) & water - “S” System
  - com. plasticizer (Zusoplast C92), com. lubricant (Zusoplast 126/3), sacarose & water - “Z” System

PROCEDURE

- Ceramic formulations made by hand kneading
  - Demineralized water
  - Solid additives in solution
  - Liquid additives
  - Solids content was set a maximum value defined by manual perception
## Formulations

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Sacarose /%(w/w)</th>
<th>PVA /%(w/w)</th>
<th>Oleic acid /%(w/w)</th>
<th>Solids loading /% (vol/vol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S_PVA_OA_1</td>
<td>6.8</td>
<td>0.3</td>
<td>3.3</td>
<td>50.9</td>
</tr>
<tr>
<td>S_PVA_OA_2</td>
<td>7.4</td>
<td>0.1</td>
<td>1.2</td>
<td>43.2</td>
</tr>
<tr>
<td>S_PVA_OA_3</td>
<td>7.8</td>
<td>0.4</td>
<td>1.3</td>
<td>46.3</td>
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<tr>
<td>S_PVA_OA_4</td>
<td>9.7</td>
<td>0.2</td>
<td>3.7</td>
<td>48.8</td>
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<tr>
<td>S_PVA_OA_5</td>
<td>9.7</td>
<td>0.4</td>
<td>1.6</td>
<td>45.7</td>
</tr>
<tr>
<td>S_PVA_OA_6</td>
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<td>0.6</td>
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<td>45.8</td>
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<tr>
<td>S_PVA_OA_7</td>
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<tr>
<td>S_PVA_OA_8</td>
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<tr>
<td>S_PVA_OA_9</td>
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<tr>
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<td>53.0</td>
</tr>
<tr>
<td>S_PVA_OA_10</td>
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<td>0.2</td>
<td>3.9</td>
<td>49.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Zusoplast C92 /%(w/w)</th>
<th>Zusoplast 126/3 /%(w/w)</th>
<th>Sacarose /%(w/w)</th>
<th>Citric acid /%(w/w)</th>
<th>Solids loading /% (vol/vol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>0.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>39.1</td>
</tr>
<tr>
<td>P_L_1</td>
<td>0.4</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
<td>47.1</td>
</tr>
<tr>
<td>P_L_2</td>
<td>0.4</td>
<td>0.3</td>
<td>-</td>
<td>-</td>
<td>49.5</td>
</tr>
<tr>
<td>P_L_3</td>
<td>1.5</td>
<td>0.3</td>
<td>-</td>
<td>-</td>
<td>49.2</td>
</tr>
<tr>
<td>P_L_4</td>
<td>1.9</td>
<td>0.3</td>
<td>-</td>
<td>-</td>
<td>42.4</td>
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<td>P_L_S_1</td>
<td>0.1</td>
<td>0.1</td>
<td>7.6</td>
<td>-</td>
<td>48.0</td>
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<tr>
<td>P_L_S_2</td>
<td>0.4</td>
<td>0.1</td>
<td>7.6</td>
<td>-</td>
<td>48.4</td>
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<tr>
<td>P_L_S_3</td>
<td>0.4</td>
<td>0.1</td>
<td>9.8</td>
<td>-</td>
<td>45.0</td>
</tr>
<tr>
<td>P_L_S_4</td>
<td>0.4</td>
<td>0.3</td>
<td>0.4</td>
<td>-</td>
<td>49.9</td>
</tr>
<tr>
<td>P_L_S_5</td>
<td>0.4</td>
<td>0.3</td>
<td>7.5</td>
<td>-</td>
<td>46.7</td>
</tr>
<tr>
<td>P_L_S_AC_1</td>
<td>0.1</td>
<td>0.7</td>
<td>4.9</td>
<td>0.1</td>
<td>45.6</td>
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<tr>
<td>P_L_S_AC_2</td>
<td>0.1</td>
<td>0.7</td>
<td>5.1</td>
<td>0.3</td>
<td>46.3</td>
</tr>
</tbody>
</table>
Assessment of formulations

Formulation behaviour assessment:

• Plasticity
• Tacking
• Stiffness
• Robocasting trails
Assessment of formulations

Formulation behaviour assessment:

- **Plasticity**
- Tacking
- Stiffness
- Robocasting trails

<table>
<thead>
<tr>
<th>Plasticity category table</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Classification</th>
<th>Description</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non compacted</td>
<td>Not possible to have an aggregated solid mass</td>
<td><img src="image" alt="Image of non compacted plasticity" /></td>
</tr>
<tr>
<td>Breaking</td>
<td>Aggregated solid mass, but not possible to mould a roll without breaking</td>
<td><img src="image" alt="Image of breaking plasticity" /></td>
</tr>
<tr>
<td>Cracking</td>
<td>Roll moulded, but it cracks when bending.</td>
<td><img src="image" alt="Image of cracking plasticity" /></td>
</tr>
<tr>
<td>Bending</td>
<td>Homogenous roll that bends without cracking</td>
<td><img src="image" alt="Image of bending plasticity" /></td>
</tr>
</tbody>
</table>
Assessment of formulations

Formulation behaviour assessment:

- Plasticity
- Tacking
- Stiffness
- Robocasting trails

<table>
<thead>
<tr>
<th>Category</th>
<th>Description</th>
<th>Image</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slightly tacky</td>
<td>It sticks slightly but it can be handle and easy to mould.</td>
<td></td>
</tr>
<tr>
<td>Tacky</td>
<td>Even sticking to the table and gloves, it is able to be moulded.</td>
<td></td>
</tr>
<tr>
<td>Highly tacky</td>
<td>The material sticks to the table and gloves, and cannot be shaped.</td>
<td></td>
</tr>
</tbody>
</table>
Não percebo o que queres dizer na última parte desta frase
luisa; 09/09/2019
Assessment of formulations

Formulation behaviour assessment:

- Plasticity
- Tacking
- **Stiffness**
- Robocasting trails

### Stiffness category table

<table>
<thead>
<tr>
<th>Category</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>●●○○○○</td>
<td>Low stiffness</td>
</tr>
<tr>
<td>●●●●○○</td>
<td>Low-Medium stiff</td>
</tr>
<tr>
<td>●●●●●●</td>
<td>Medium-high stiff</td>
</tr>
<tr>
<td>●●●●●●</td>
<td>Stiff</td>
</tr>
</tbody>
</table>
Assessment of formulations

Formulation behaviour assessment:

• Plasticity
• Tacking
• Stiffness
• Robocasting trials

Printing performance evaluation topics:

- Constant flow through the extrusion nozzle
- First layer sticking of the extrudate to the building platform
- Layer by layer sticking
- Side extrudate sticking
- Structural integrity of the building form

Good part => good formulation behaviour
### Assessment results

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Sacarose /%(w/w)</th>
<th>PVA /%(w/w)</th>
<th>Oleic acid /%(w/w)</th>
<th>Solids loading / % (vol/vol)</th>
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<th>Stiffness</th>
<th>Printing tested?</th>
</tr>
</thead>
<tbody>
<tr>
<td>S_PVA_OA_1</td>
<td>6.8</td>
<td>0.3</td>
<td>3.3</td>
<td>50.9</td>
<td>●●●●●●●●●●</td>
<td>○○○○○○○○○○</td>
<td>○○○○○○○○○○</td>
<td></td>
</tr>
<tr>
<td>S_PVA_OA_2</td>
<td>7.4</td>
<td>0.1</td>
<td>1.2</td>
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</tr>
<tr>
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<tr>
<td>S_PVA_OA_5</td>
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<tr>
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<td>2.2</td>
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<tr>
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<td>-</td>
<td>48.0</td>
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<td>48.4</td>
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<td>P_L_S_4</td>
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<td>0.3</td>
<td>7.5</td>
<td>-</td>
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<td>0.7</td>
<td>4.9</td>
<td>0.1</td>
<td>45.3</td>
<td>●●●●●●●●●●</td>
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<td>○○○○○○○○○○</td>
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</tbody>
</table>
## Phase 2 - Robocasting and characterization

**Plastic body compounding** → **Printing** → **Debinding and Sintering**

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Alumina size, D50 /µm</th>
<th>Sacarose /%(w/w)</th>
<th>PVA /%(w/w)</th>
<th>Oleic acid /%(w/w)</th>
<th>Solids loading / % (vol/vol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S_PVA_OA_9</td>
<td>0.4</td>
<td>9.9</td>
<td>0.4</td>
<td>2.2</td>
<td>47.6</td>
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<tr>
<td>S_PVA_OA_9+</td>
<td>4</td>
<td>9.9</td>
<td>0.4</td>
<td>2.2</td>
<td>53.0</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Alumina size, D50 /µm</th>
<th>Zusoplast C92 /%(w/w)</th>
<th>Zusoplast 126/3 /%(w/w)</th>
<th>Sacarose /%(w/w)</th>
<th>Citric acid /%(w/w)</th>
<th>Solids loading / % (vol/vol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P_L_S_5</td>
<td>0.4</td>
<td>0.4</td>
<td>0.3</td>
<td>7.5</td>
<td>-</td>
<td>46.7</td>
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<tr>
<td>P_L_S_AC_1</td>
<td>0.4</td>
<td>0.1</td>
<td>0.7</td>
<td>4.9</td>
<td>0.1</td>
<td>45.6</td>
</tr>
</tbody>
</table>
Phase 2 - Robocasting and characterization

- Plastic body compounding
- Printing
- Debinding and Sintering

- Rheology: Rotational shear rheometry with a Haake Rheotress 1
- Hardness: Indentation force measurement with a Geotester Penetrometer
Phase 2 - Robocasting and characterization

**Cura Parameters**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Version</td>
<td>V2.3.1</td>
</tr>
<tr>
<td>Nozzle diameter / mm</td>
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<tr>
<td>Layer thickness / mm</td>
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<tr>
<td>First layer thickness / mm</td>
<td>0.5</td>
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<tr>
<td>Wall printing speed / mm.s⁻¹</td>
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</tr>
<tr>
<td>Fill printing speed / mm.s⁻¹</td>
<td>30</td>
</tr>
<tr>
<td>Bottom and top printing speed / mm.s⁻¹</td>
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<tr>
<td>Travel speed / mm.s⁻¹</td>
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</tr>
<tr>
<td>Flow /%</td>
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</tr>
<tr>
<td>Wall thickness / mm</td>
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</tr>
<tr>
<td>Wall line counts / -</td>
<td>3</td>
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<tr>
<td>Bottom and top thickness / mm</td>
<td>3</td>
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<tr>
<td>Fill density / %</td>
<td>100</td>
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</tbody>
</table>
Phase 2 - Robocasting and characterization

1. Plastic body compounding
2. Printing
3. Debinding and Sintering

- Porosity: Arquimedes principle
- Flexure strength: 3-point flexure testing
Rheology of the formulations

Rheometer procedure issues faced calling for patience work:
- High normal force before reach the gap programmed (stiff formulations)
- Slip-stick behaviour suspected (high filled suspensions)
- Sample spreading

Test conditions: Parallel plates geometry R=10mm; Gap h=0.5mm
Rheology of the formulations

Test conditions: Parallel plates geometry $R=10\text{mm}; \text{Gap } h=0.5\text{mm}$

- Pseudoplastic behaviour of both formulations
- Formulation with higher particle size shows lower viscosity, despite having a higher solids loading
Rheology of the formulations

- Pseudoplastic behaviour of both formulations
- Slightly difference between viscosity of the two formulations

Test conditions: Parallel plates geometry R=10mm; Gap h=0.5mm
Rheology of the formulations

- Thixotropic behaviour

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Powder D50</th>
<th>Sacarose</th>
<th>PVA</th>
<th>Oleic acid</th>
<th>Solids loading</th>
</tr>
</thead>
<tbody>
<tr>
<td>S_PVA_OA_9</td>
<td>0.4</td>
<td>9.9</td>
<td>0.4</td>
<td>2.2</td>
<td>47.6</td>
</tr>
<tr>
<td>S_PVA_OA_9+</td>
<td>4</td>
<td>9.9</td>
<td>0.4</td>
<td>2.2</td>
<td>53.0</td>
</tr>
</tbody>
</table>
Rheology of the formulations

- Non-thixotropic behaviour

- Thixotropic behaviour

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Powder D50 /µm</th>
<th>C92 /% (w/w)</th>
<th>126/3 /% (w/w)</th>
<th>Sacarose /% (w/w)</th>
<th>Citric acid /% (w/w)</th>
<th>Solids loading /% (vol/vol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P_L_S_5</td>
<td>0.4</td>
<td>0.4</td>
<td>0.3</td>
<td>7.5</td>
<td>-</td>
<td>46.7</td>
</tr>
<tr>
<td>P_L_S_AC_1</td>
<td>0.4</td>
<td>0.1</td>
<td>0.7</td>
<td>4.9</td>
<td>0.1</td>
<td>45.6</td>
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</table>
Rheology and hardness of the formulations

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Hardness /kg</th>
<th>Viscosity in 0.5-20 s⁻¹ range /Pa.s</th>
<th>Printing behaviour</th>
</tr>
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<tbody>
<tr>
<td>S_PVA_OA_9</td>
<td>1.8</td>
<td>91 to 4349</td>
<td>Poor adhesion to the building platform</td>
</tr>
<tr>
<td>S_PVA_OA_9+</td>
<td>&lt; 1</td>
<td>17 to 3187</td>
<td>Prints well</td>
</tr>
<tr>
<td>P_L_S_5</td>
<td>-</td>
<td>159 to 11195</td>
<td>-</td>
</tr>
<tr>
<td>P_L_S_AC_1</td>
<td>2.9</td>
<td>159 to 8870</td>
<td>Prints with upper limit reservoir pressure</td>
</tr>
</tbody>
</table>

- Formulation hardness is proportional to viscosity
- Formulations with hardness higher than ca. 3 kg are not recommended for processing
Sintered porosity and bending strength

- Higher porosity (33 & 37%) in formulation based on higher powder particle size (D50 = 4µm)
- Higher strength in sintered formulations with lower porosity

**Total Porosity**

![Bar chart showing total porosity](image)

**Bending Strength**

![Bar chart showing bending strength](image)
Prototype production

Formulation S_PVA_OA_9+

Formulation P_L_S_AC_1

Green: 15x15x4mm

Green: 16x16x10mm
Sintering linear shrinkage

Higher shrinkage in formulations with lower particle size and high densification (S_P_OA_9 and P_L_S_AC_1)

Higher shrinkage in Z direction

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Plate</th>
<th></th>
<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>$R_{L,x}$ /%</td>
<td>$R_{L,y}$ /%</td>
<td>$R_{L,z}$ /%</td>
<td>$R_{L,D}$ /%</td>
<td>$R_{L,d}$ /%</td>
<td>$R_{L,H}$ /%</td>
<td>$R_{L,h}$ /%</td>
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<tr>
<td>S_P_OA_9</td>
<td>17,7</td>
<td>18,3</td>
<td>17,6</td>
<td>18,4</td>
<td>17,3</td>
<td>20,2</td>
<td>19,3</td>
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<tr>
<td>S_P_OA_9+</td>
<td>4,8</td>
<td>4,6</td>
<td>6,0</td>
<td>3,8</td>
<td>3,9</td>
<td>6,8</td>
<td>7,4</td>
</tr>
<tr>
<td>P_L_S_AC_1</td>
<td>18</td>
<td>18,55</td>
<td>25,5</td>
<td>18,2</td>
<td>16,4</td>
<td>21,8</td>
<td>18,9</td>
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Application prototyping

Formulation S_PVA_OA_9 (alumina D=0.4μm)

printing a gas dosing valve disc
Application prototyping

Green parts:
- Injection moulding (left)
- Robocasting (right)

- Green parts (top)
- Sintered parts (bottom)
Conclusion

• Comparing to AM of plastics and metals, ceramics are in the very beginning but with a huge potential

• Technology and application should be developed together
Thank you