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Processing of alumina suspensions by robocasting

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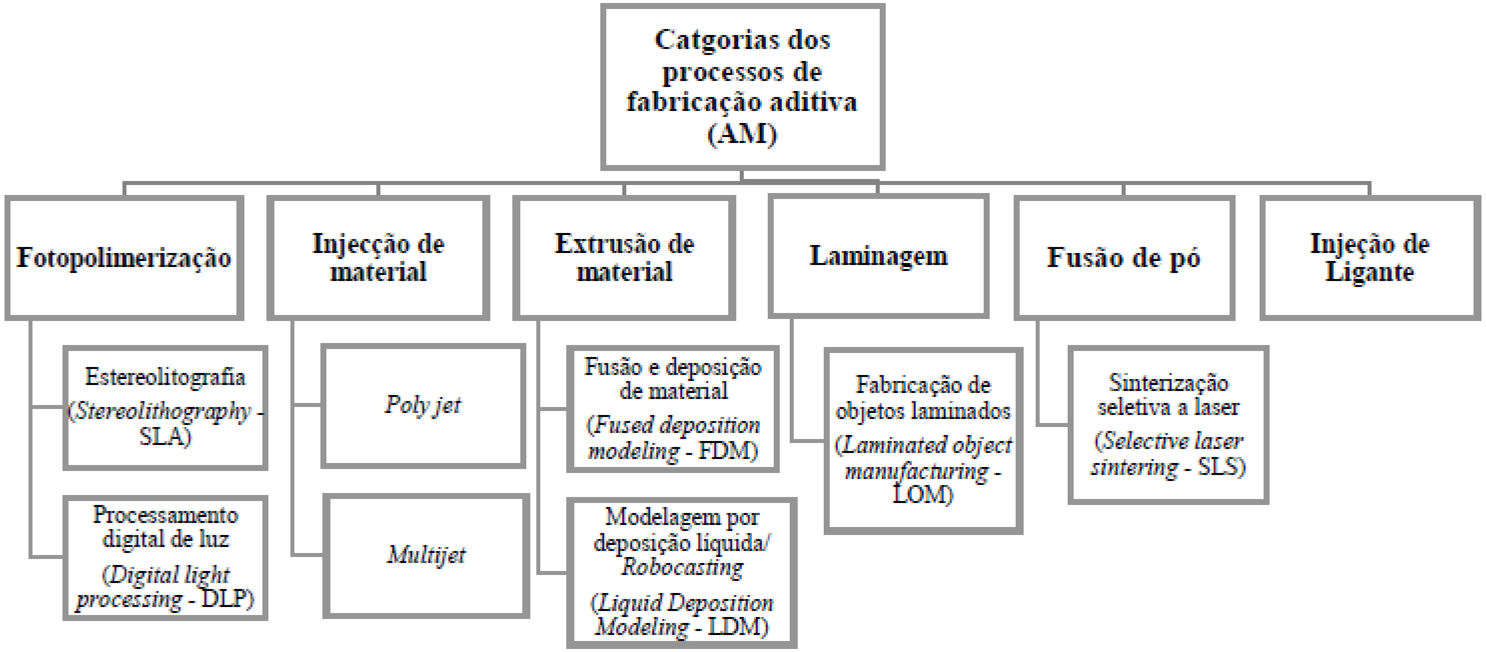
Additive manufacturing of structural ceramics

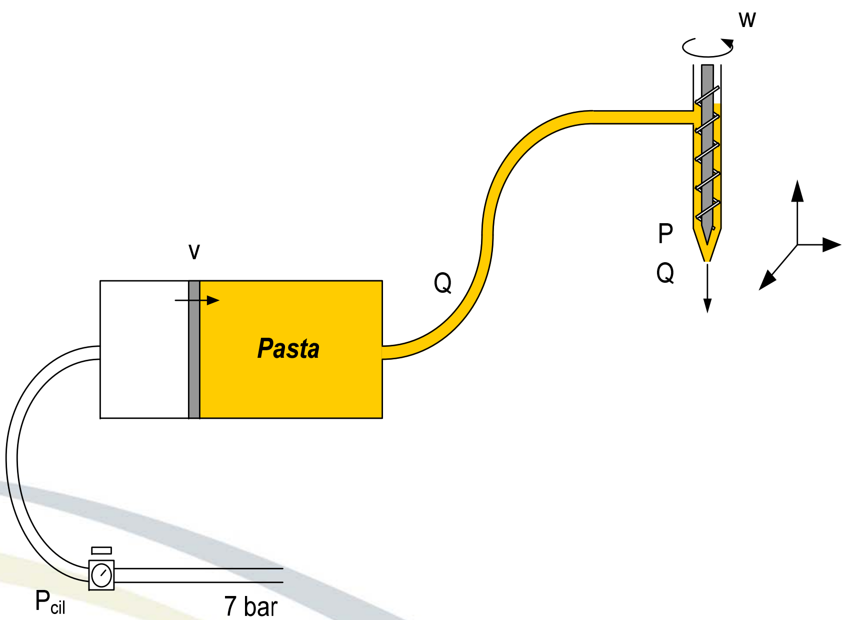


- Photopolimerization based methods
  - high final shape precision
  - small size parts
  - high densification materials
  - but available at a high investment cost
- Robocasting / LDM
  - medium shape precision or pre-forms
  - higher size parts
  - access at with low/medium investment cost

Study goals

- To evaluate of the printability of alumina compounds by robocasting
- To study the effect of:
  - Powder particle size of raw material
  - Solids content of the ceramic body
  - Processing additives of the ceramic body

Robocasting system used



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 as the maximum as possible defined by manual perception

Formulations

Formulation	Sacarose /%(w/w)	PVA /%(w/w)	Oleic acid /%(w/w)	Solids loading / % (vol/vol)
S_PVA_OA_1	6.8	0.3	3.3	50.9
S_PVA_OA_2	7.4	0.1	1.2	43.2
S_PVA_OA_3	7.8	0.4	1.3	46.3
S_PVA_OA_4	9.7	0.2	3.7	48.8
S_PVA_OA_5	9.7	0.4	1.6	45.7
S_PVA_OA_6	9.8	0.6	2.2	45.8
S_PVA_OA_7	9.9	0.2	2.0	48.2
S_PVA_OA_8	9.9	0.4	2.0	48.1
S_PVA_OA_9	9.9	0.4	2.2	47.6
S_PVA_OA_9+	9.9	0.4	2.2	53.0
S_PVA_OA_10	11.5	0.2	3.9	49.9

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

Assessment of formulations

Formulation behaviour assessment:

- Plasticity
- Tacking
- Stiffness
- Robocasting trails

Assessment of formulations

Formulation behaviour assessment:

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

Plasticity category table

Classification	Description	Example
●○○○ Non compacted	Not possible to have an aggregated solid mass	
●●●○○○ Breaking	Aggregated solid mass, but not possible to mould a roll without breaking	
●●●●●○ Cracking	Roll moulded, but it cracks when bending.	
●●●●●● Bending	Homogenous roll that bends without cracking	

Assessment of formulations

Formulation behaviour assessment:

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

Tacking category table

Category	Description	Image
●○○○○ Slightly tacky	It sticks slightly but it can be handle and easy to mould.	
●●●●○○ Tacky	Even sticking to the table and gloves, it is able to be moulded	
●●●●●● Highly tacky	The material sticks to the table and gloves, and cannot be shaped I6	

Diapositivo 9

I6 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

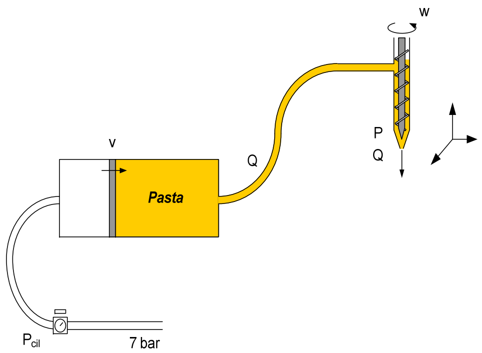
Stiffness category table

Category	Description
●○○○○○	Low stiffness
●●○○○○	Low-Medium stiff
●●●●○○	Medium-high stiff
●●●●●●	Stiff

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

Formulation	Sacarose /%(w/w)	PVA /%(w/w)	Oleic acid /%(w/w)	Solids loading / % (vol/vol)	Plasticity	Tacking	Stiffness	Printing tested?
S_PVA_OA_1	6.8	0.3	3.3	50.9	●●○○○○	○○○○○○	○○○○○○	
S_PVA_OA_2	7.4	0.1	1.2	43.2	○○○○○○	○○○○○○	○○○○○○	
S_PVA_OA_3	7.8	0.4	1.3	46.3	●●●○○○	○○○○○○	●●●●○○	
S_PVA_OA_4	9.7	0.2	3.7	48.8	●●●○○○	○○○○○○	○○○○○○	Yes
S_PVA_OA_5	9.7	0.4	1.6	45.7	●○○○○○	○○○○○○	○○○○○○	
S_PVA_OA_6	9.8	0.6	2.2	45.8	●●●●○○	○○○○○○	●●●●○○	
S_PVA_OA_7	9.9	0.2	2.0	48.2	●●●●○○	○○○○○○	●○○○○○	Yes
S_PVA_OA_8	9.9	0.4	2.0	48.1	●●●●●○	●○○○○○	○○○○○○	Yes
S_PVA_OA_9	9.9	0.4	2.2	47.6	●●●●○○	○○○○○○	●○○○○○	
S_PVA_OA_9+	9.9	0.4	2.2	53.0	●●●●●○	●○○○○○	●●○○○○	
S_PVA_OA_10	11.5	0.2	3.9	49.9	●○○○○○	○○○○○○	○○○○○○	

Formulation	*Zusoplast C92* /%(w/w)	*Zusoplast 126/3* /%(w/w)	Sacarose /%(w/w)	Citric acid /%(w/w)	Solids loading / % (vol/vol)	Plasticity	Tacking	Stiffness	Printing tested?
P	0.4	-	-	-	39.1	●●●●●●	●●●●●●	○○○○○○	Yes
P_L_1	0.4	0.1	-	-	47.1	●●●●●●	○○○○○○	●●●●●●	
P_L_2	0.4	0.3	-	-	49.5	●●●●●●	●●●○○○	●●○○○○	
P_L_3	1.5	0.3	-	-	49.2	●●●●○○	●○○○○○	●●●●●●	
P_L_4	1.9	0.3	-	-	42.4	●●●●●●	●●●●●●	○○○○○○	
P_L_S_1	0.1	0.1	7.6	-	48.0	●●●●●●	●●●○○○	●●○○○○	
P_L_S_2	0.4	0.1	7.6	-	48.4	●●●●●●	○○○○○○	●●●●●○	
P_L_S_3	0.4	0.1	9.8	-	45.0	●●●●●○	●●●●●●	●●●○○○	
P_L_S_4	0.4	0.3	0.4	-	49.9	●●●●○○	○○○○○○	●●●●○○	
P_L_S_5	0.4	0.3	7.5	-	46.7	●●●●●●	●●●●○○	●●●○○○	
P_L_S_AC_1	0.1	0.7	4.9	0.1	45.6	●●●●○○	●●●○○○	●●○○○○	Yes
P_L_S_AC_2	0.1	0.7	5.1	0.3	46.3	●●●●●●	●●●○○○	●●○○○○	Yes

Phase 2 – Robocasting and characterization

Plastic body compounding → Printing → Debinding and Sintering

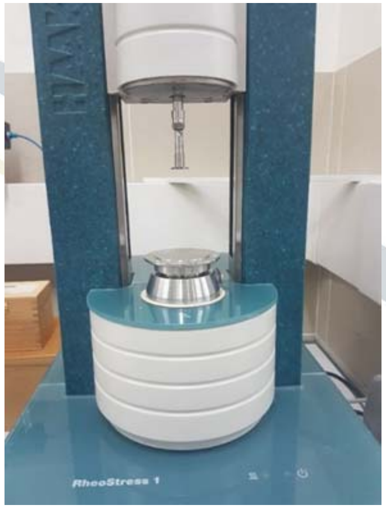
Formulation	Alumina size, D50 /µm	Sacarose /%(w/w)	PVA /%(w/w)	Oleic acid /%(w/w)	Solids loading / % (vol/vol)
S_PVA_OA_9	0.4	9.9	0.4	2.2	47.6
S_PVA_OA_9+	4	9.9	0.4	2.2	53.0

Formulation	Alumina size, D50 /µm	*Zusoplast C92* /%(w/w)	*Zusoplast 126/3* /%(w/w)	Sacarose /%(w/w)	Citric acid /%(w/w)	Solids loading / % (vol/vol)
P_L_S_5	0.4	0.4	0.3	7.5	-	46.7
P_L_S_AC_1	0.4	0.1	0.7	4.9	0.1	45.6

Phase 2 – Robocasting and characterization

Plastic body compounding → Printing → Debinding and Sintering

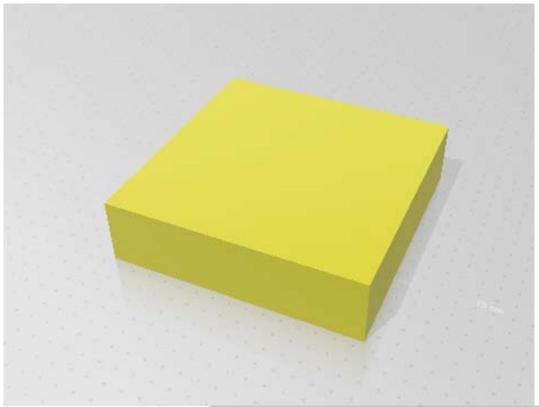
- Rheology — Rotational shear rheometry with a Haake Rheotress 1
- Hardness — Indentation force measurement with a Geotester Penetrometer

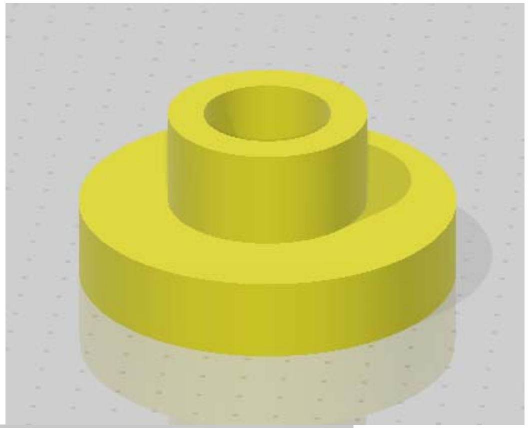


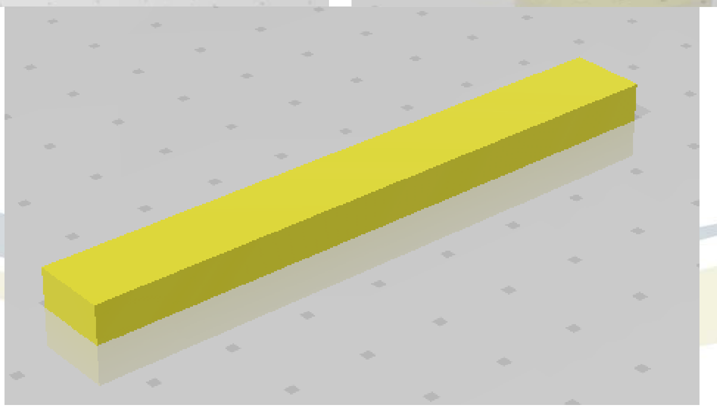
Phase 2 – Robocasting and characterization

Plastic body compounding → Printing → Debinding and Sintering

Cura Parameters	
Version	V2.3.1
Nozzle diameter / mm	1
Layer thickness /mm	0,7
First layer thickness /mm	0,5
Wall printing speed /mm.s^{-1}	30
Fill printing speed /mm.s^{-1}	30
Bottom and top printing speed /mm.s^{-1}	30
Travel speed /mm.s^{-1}	60
Flow /%	100
Wall thcikness /mm	3
Wall line counts/ -	3
Bottom and top thickness /mm	3
Fill density /%	100





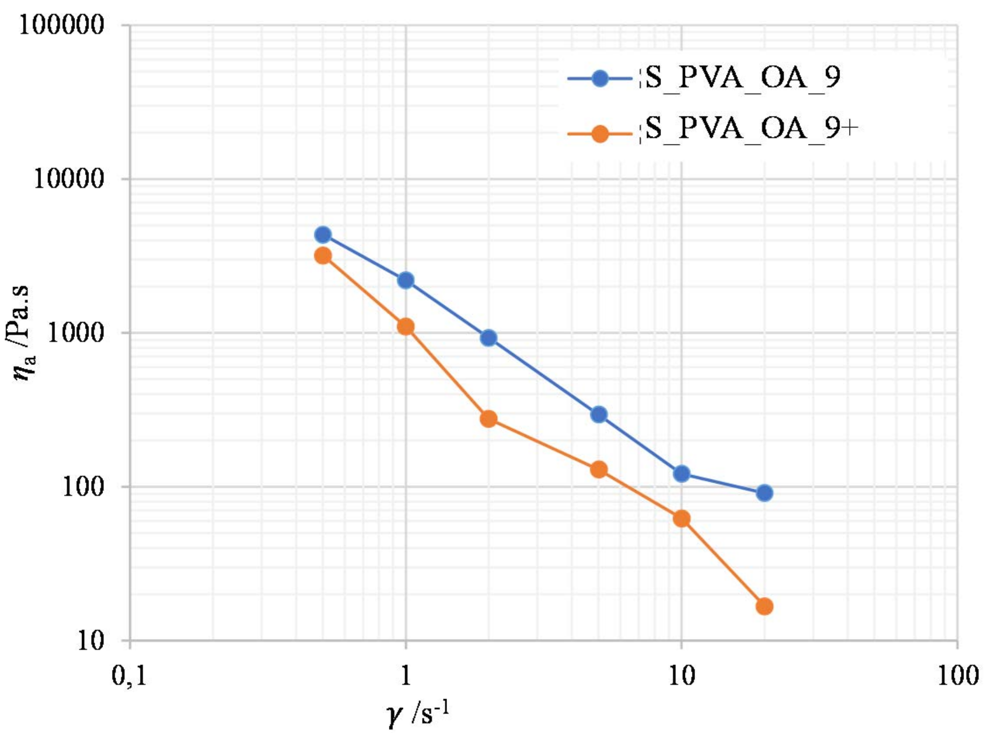


Phase 2 – Robocasting and characterization

Plastic body compounding → Printing → Debinding and Sintering

- Porosity	Arquimedes principle
- Flexural strength	3-point flexural testing

Rheology of the formulations

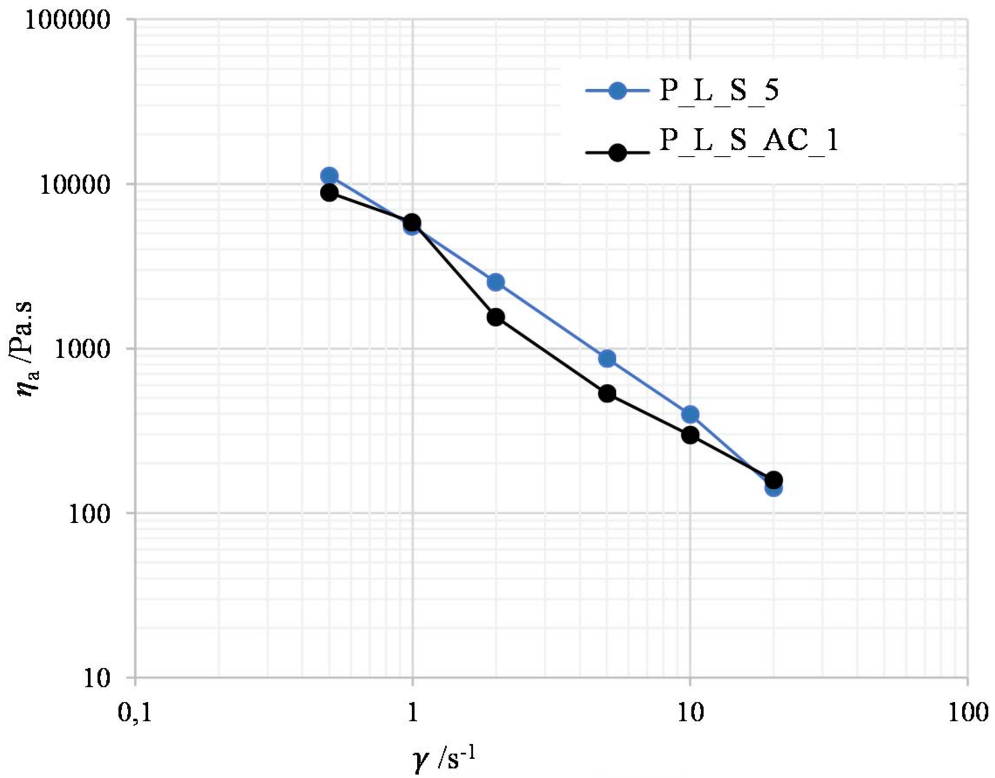


Formulation	Powder D50 /µm	Sacarose /%(w/w)	PVA /%(w/w)	Oleic acid /%(w/w)	Solids loading / % (vol/vol)
S_PVA_OA_9	0.4	9.9	0.4	2.2	47.6
S_PVA_OA_9+	4	9.9	0.4	2.2	53.0

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

Test conditions: Parallel plates geometry R=10mm; Gap h=0.5mm

Rheology of the formulations



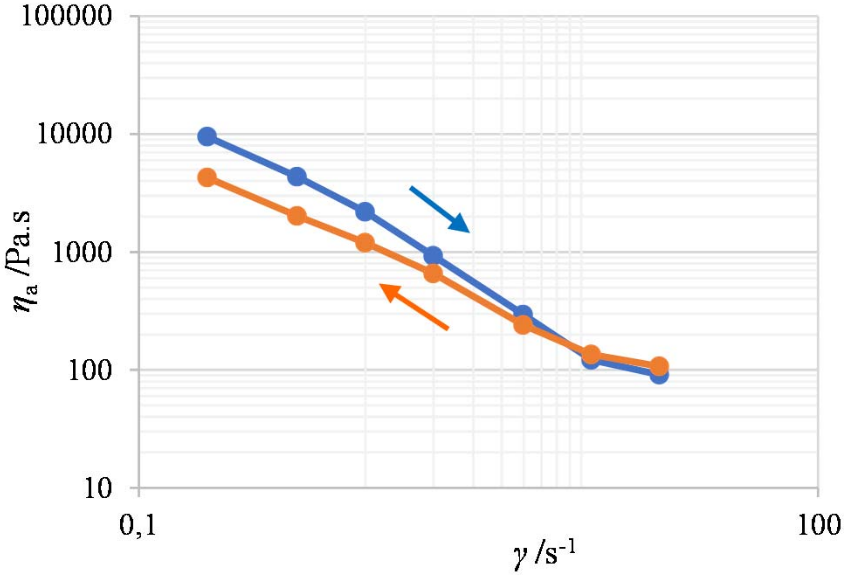
Formulation	Powder D50 /µm	*C92* /%(w/w)	*126/3* /%(w/w)	Sacarose /%(w/w)	Citric acid /%(w/w)	Solids loading / % (vol/vol)
P_L_S_5	0.4	0.4	0.3	7.5	-	46.7
P_L_S_AC_1	0.4	0.1	0.7	4.9	0.1	45.6

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

Test conditions: Parallel plates geometry R=10mm; Gap h=0.5mm

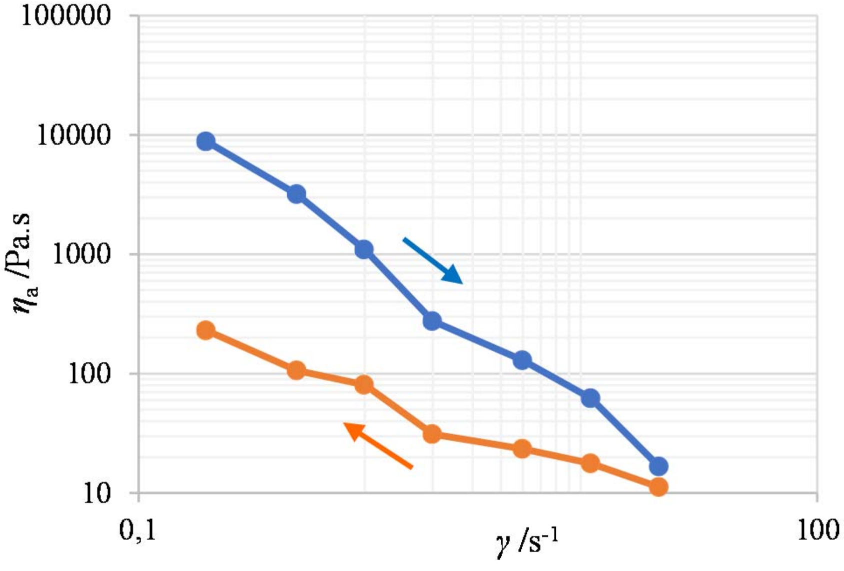
Rheology of the formulations

S_PVA_OA_9



- Thixotropic behaviour

S_PVA_OA_9+

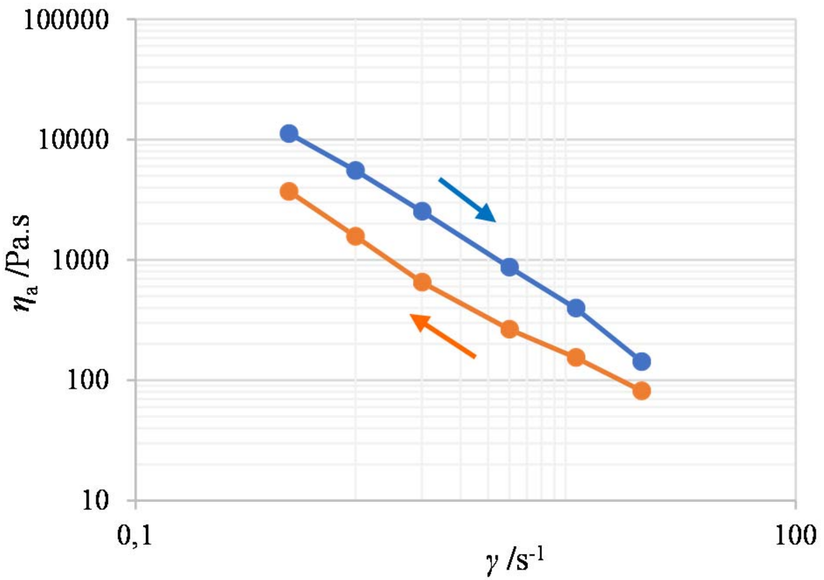


- Thixotropic behaviour

Formulation	Powder D50 /µm	Sacarose /%(w/w)	PVA /%(w/w)	Oleic acid /%(w/w)	Solids loading / % (vol/vol)
S_PVA_OA_9	0.4	9.9	0.4	2.2	47.6
S_PVA_OA_9+	4	9.9	0.4	2.2	53.0

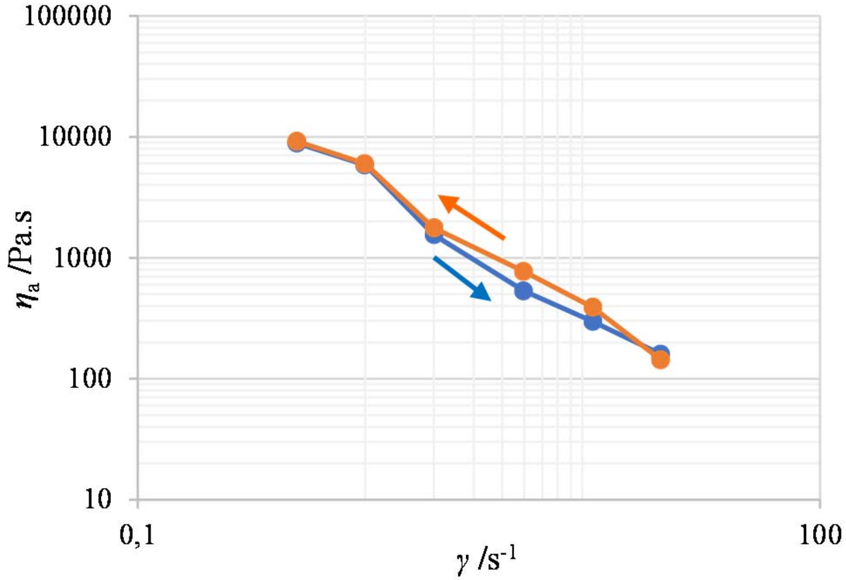
Rheology of the formulations

P_L_S_5



- Thixotropic behaviour

P_L_S_AC_1



- Non-thixotropic behaviour

Formulation	Powder D50 /µm	*C92* /%(w/w)	*126/3* /%(w/w)	Sacarose /%(w/w)	Citric acid /%(w/w)	Solids loading / % (vol/vol)
P_L_S_5	0.4	0.4	0.3	7.5	-	46.7
P_L_S_AC_1	0.4	0.1	0.7	4.9	0.1	45.6

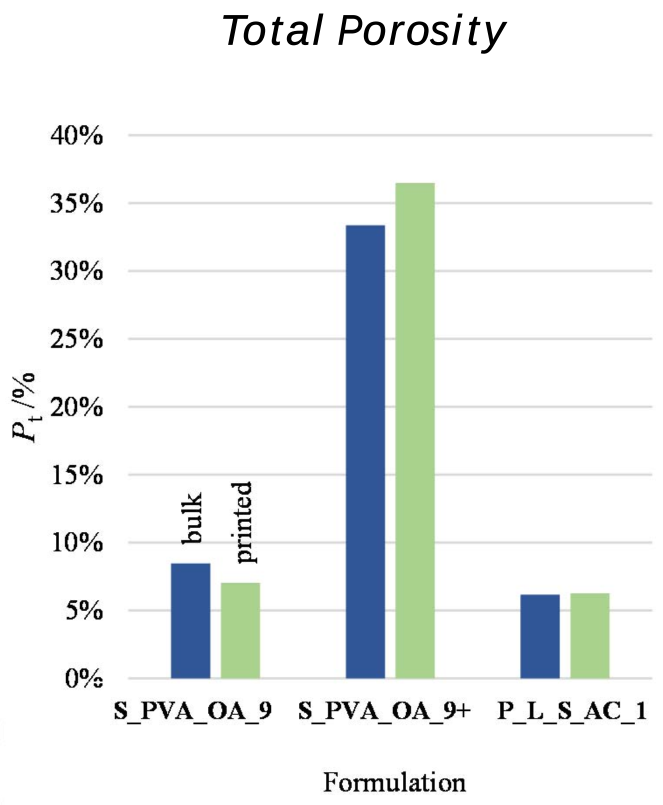
Rheology and hardness of the formulations

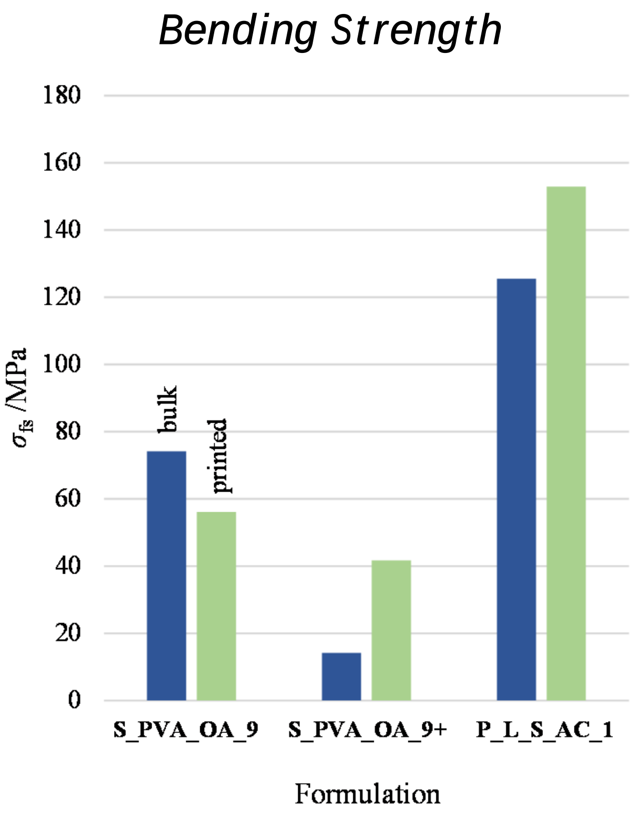
Formulation	Hardness /kg	Viscosity in 0,5-20 s^{-1} range /Pa.s	Printing behaviour
S_PVA_OA_9	1,8	91 to 4349	Poor adhesion to the building platform
S_PVA_OA_9+	< 1	17 to 3187	Prints well
P_L_S_5	-	159 to 11195	-
P_L_S_AC_1	2,9	159 to 8870	Prints with upper limit reservoir pressure

Hardness test indenter of D=20mm

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

Sintered porosity and bending strength





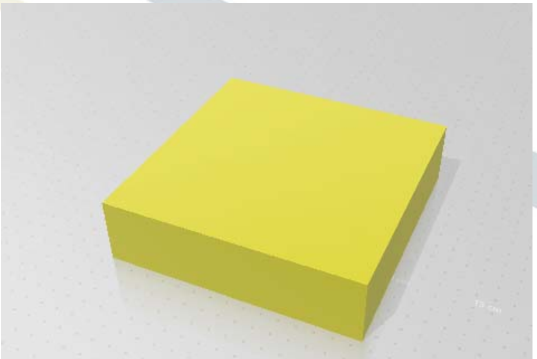
Sintering conditions: 5 ºC/min - 1600ºC - 2h

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

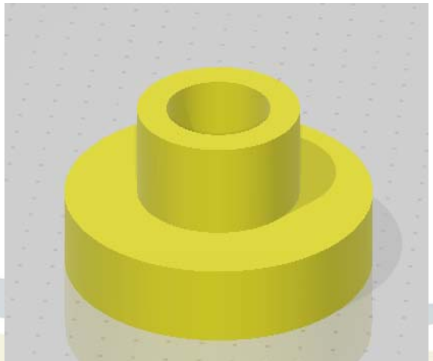
Prototype production

Formulation S_PVA_OA_9+

Formulation P_L_S_AC_1



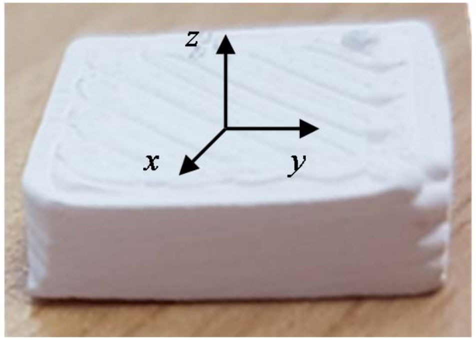
Green: 15x15x4mm



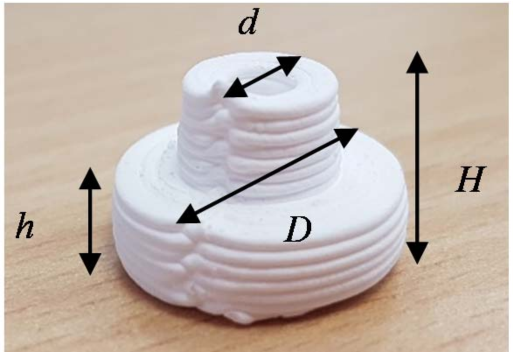
Green: 16x16x10mm

Sintering linear shrinkage

Plate



Spacer

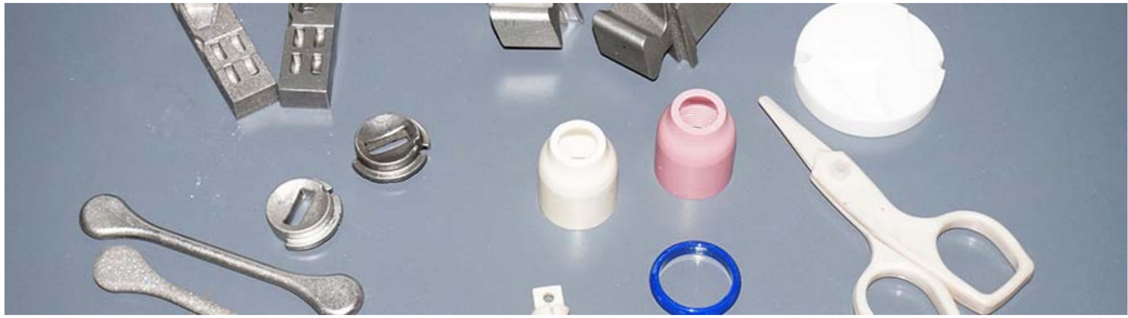


Formulation	Plate			Spacer			
	$R_{L,x}$ /%	$R_{L,y}$ /%	$R_{L,z}$ /%	$R_{L,D}$ /%	$R_{L,d}$ /%	$R_{L,H}$ /%	$R_{L,h}$ /%
S_P_OA_9	17,7	18,3	17,6	18,4	17,3	20,2	19,3
S_P_OA_9+	4,8	4,6	6,0	3,8	3,9	6,8	7,4
P_L_S_AC_1	18,	18,55	25,5	18,2	16,4	21,8	18,9

- 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

Conclusions

- In the 1st part of the study, a high range of alumina formulations for robocasting were prepared and evaluated in terms of empirical topics (plasticity, tacking, stiffness and robocasting trials)
- In the 2^{nd} part of the study, the best promise formulation were then characterized and processed.
- Formulations show shear-thinning behaviour and some of them are substantially thixotropic
- Some process constraints were found, such as, high feeding pressure or extrudate deposition problems.
- Hardness and viscosity of formulation upper limits were found for processing with the WASP 2040 printer.
- Printing processing is viable as the sintered printed material properties were similar to sintered bulk paste.
- Coarse alumina formulation has been printed well, for high porosity applications.
- Fine alumina formulation needs to be optimized in order to decrease de machine feed pressure as well as extrusion stability.



Thank you

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