University of Birmingham
College of Engineering and Physical Sciences
School of Metallurgy and Materials

Additive manufacturing of ceramic powders and their composites for bone repair

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Outline

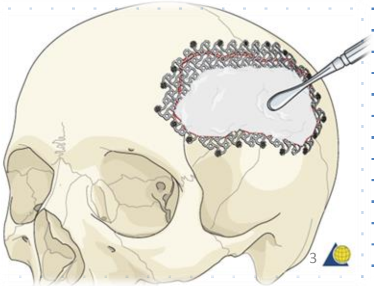
- Background
    - ✓ Bone transplantation (Reasons and Methods)
    - ✓ Features of scaffolds for bone repair
    - ✓ Synthetic Biomaterials
    - ✓ Fabrication techniques of scaffolds
    - ✓ Additive manufacturing
- Aims of the project
- Experimental procedures
- Results and discussion
- Conclusions
- Future Work

Background: Bone transplantation

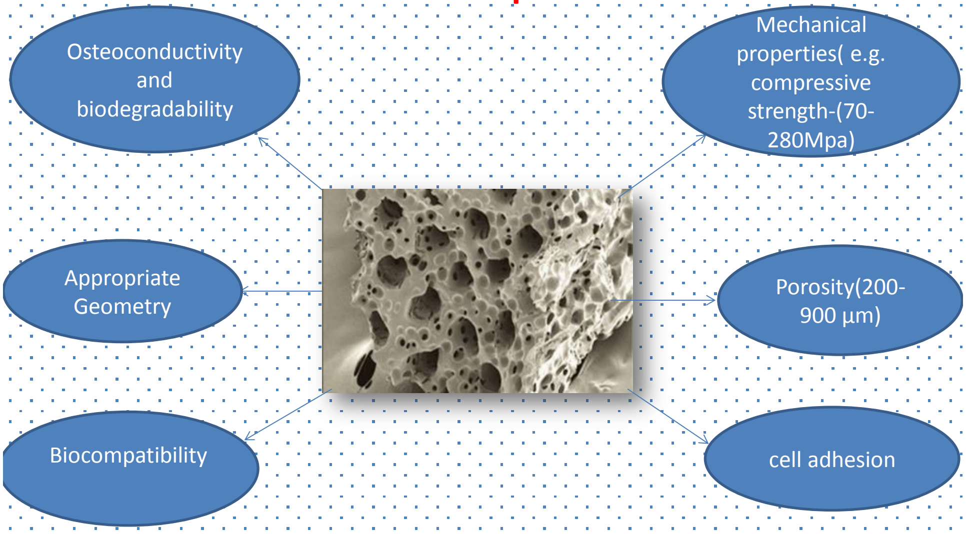
❖ Bone defects due to :Trauma, injury and accidents

- ✓ Autograft (patient's own body)
  - Requirement of a secondary surgery
  - Chronic pain at donor site
  - Long operating time
- ✓ Allograft (from donors)
  - Disease transmission
  - Limited bone availability
  - Anatomical limitation

- ✓ Artificial implants (synthetic materials)



Background: Required features of Scaffolds for bone repair



Osteoconductivity and biodegradability

Mechanical properties(e.g. compressive strength-(70-280Mpa)

Appropriate Geometry

Porosity(200-900 µm)

Biocompatibility

cell adhesion

- http://www.doitpoms.ac.uk/tlplib/bones/bone_mechanical.php

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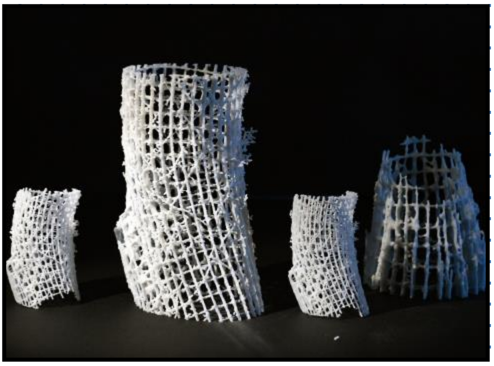
Background: Artificial Scaffolds (Synthetic Materials)

- Ceramics (e.g. HA and other Calcium phosphate phases [CaP])
- Polymers (e.g. PLA, collagen)
- Metals (e.g. Ti and Ti alloys e.g., Ti6Al4V, CoCr)
- Composites (e.g. PLA and HA)



http://horizon-magazine.eu/sites/default/files/styles/large-timeline/public/480x350xBio-scaffolds_0.jpg,qitok=VgjWtWnV.pagespeed.ic.ilUy3Na-Tv.jpg

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Background: Different Fabrication techniques

Technique	Advantages	Shortcomings
Gas foaming	• No need for organic solvents and high temperature • no harmful residues after finishing the process	• Inadequate mechanical properties • no interconnected structures among pores
Solvent casting	• Adequate porosity and crystallinity	• Toxic residuals from solvents • Poor mechanical properties
Electrospinning	• structures can be created in different dimensions and chemical properties	• Poor mechanical properties
Freeze drying	• No need for high temperatures	• Time -consuming
Additive Manufacturing(AM)	• Control over Porosity and geometry(Complex models) • No post-processing (Short time) • No requirement for mould or specific tooling	• Limited materials for processing • AM devices could be expensive

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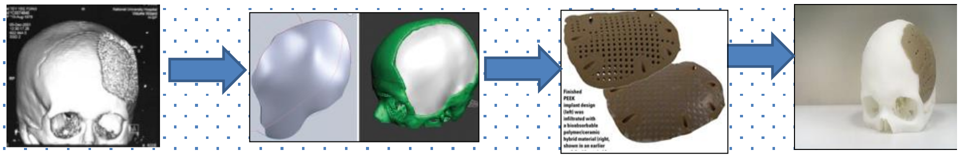
Background: Additive Manufacturing (Rapid prototyping (RP))

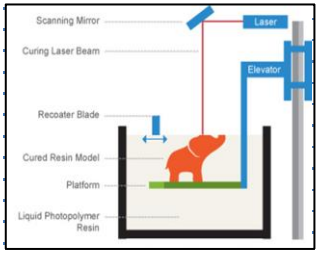
CT Scan of Bone defect → **Design** geometry and material selection (CAD) → **3-D printing** (STL file) → **Implantation**



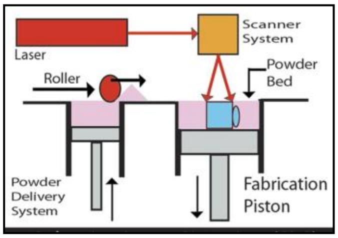
Schematic diagram of RP
Method in Making scaffold
for bone repair

Background: Different Types of RP Systems

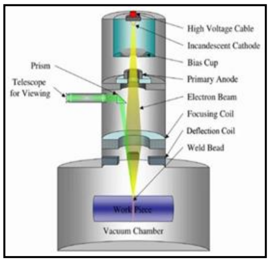
Stereolithography(SLA)

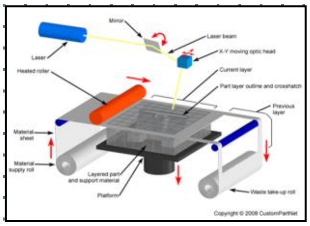


Selective laser Sintering/melting(SLS/M)

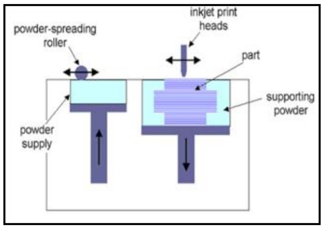


Electronic Beam Melting (EBM)

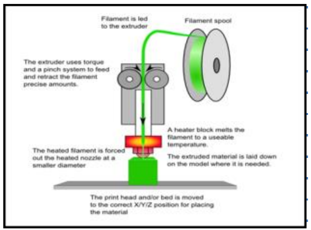




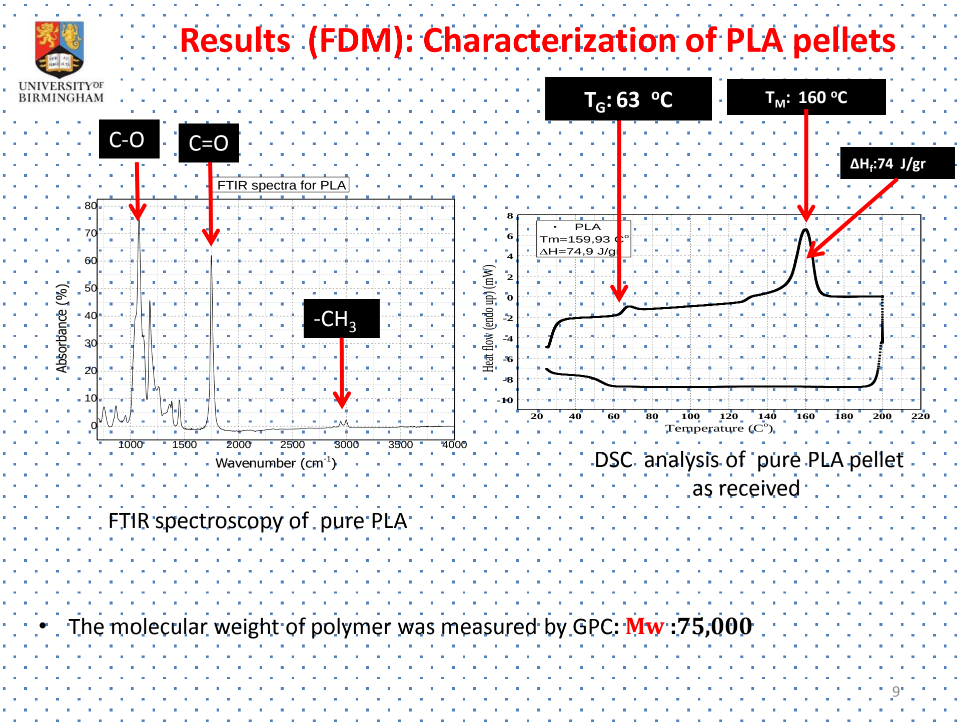
Laminated Object Manufacture (LOM)



3-D Ink-jet printing



Fused deposition modelling(FDM)



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Results (FDM): Characterization of PLA pellets

C-O

C=O

-CH_3

T_G: 63 °C

T_M: 160 °C

ΔH_f:74 J/gr

FTIR spectroscopy of pure PLA

DSC analysis of pure PLA pellet as received

- The molecular weight of polymer was measured by GPC: **Mw** :75,000

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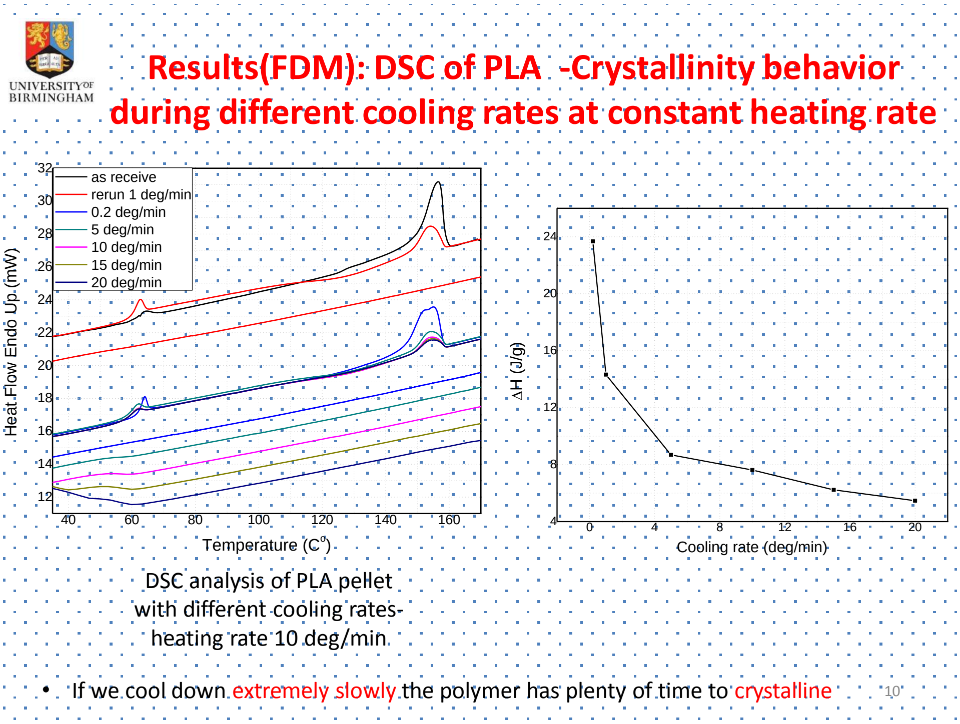

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Results(FDM): DSC of PLA -Crystallinity behavior during different cooling rates at constant heating rate

DSC analysis of PLA pellet with different cooling rates- heating rate 10 deg/min

- If we cool down extremely slowly the polymer has plenty of time to crystalline

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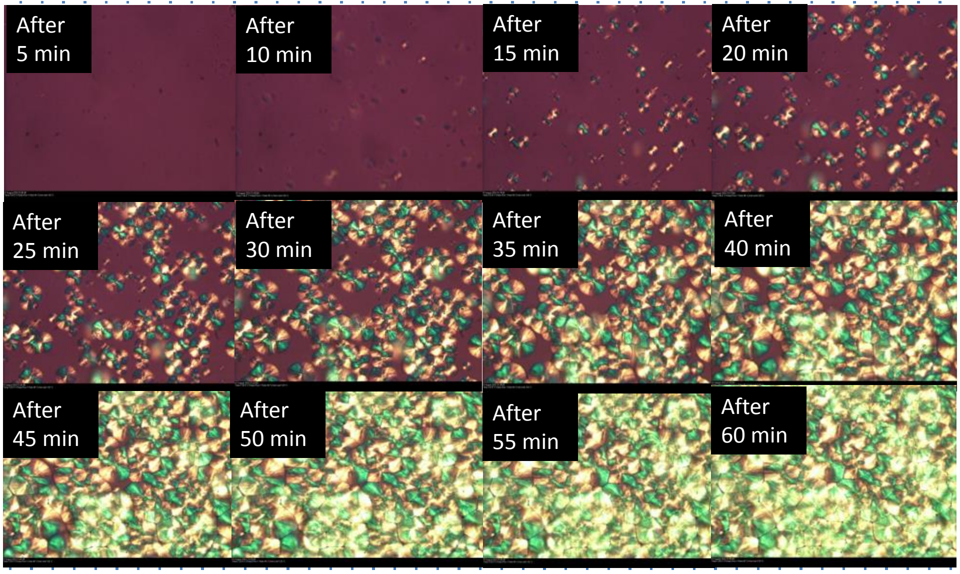
Results (FDM): Hot-Stage- cooling from 180 ^{o}C (melting point) to 120 ^{o}C



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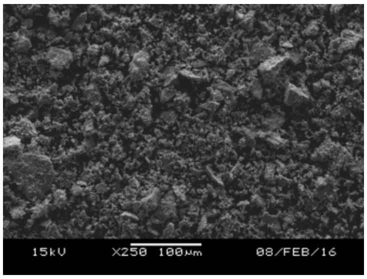
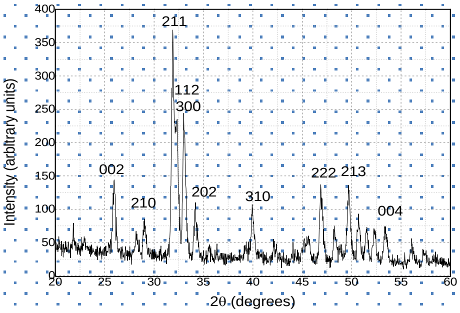
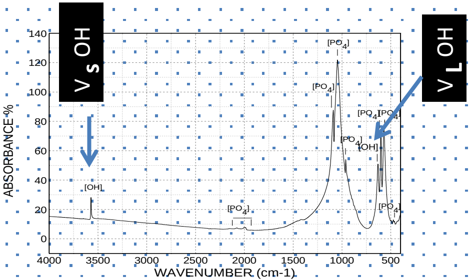
Results (FDM)- Characterization of HA powders



SEM pictures of as-received HA powders

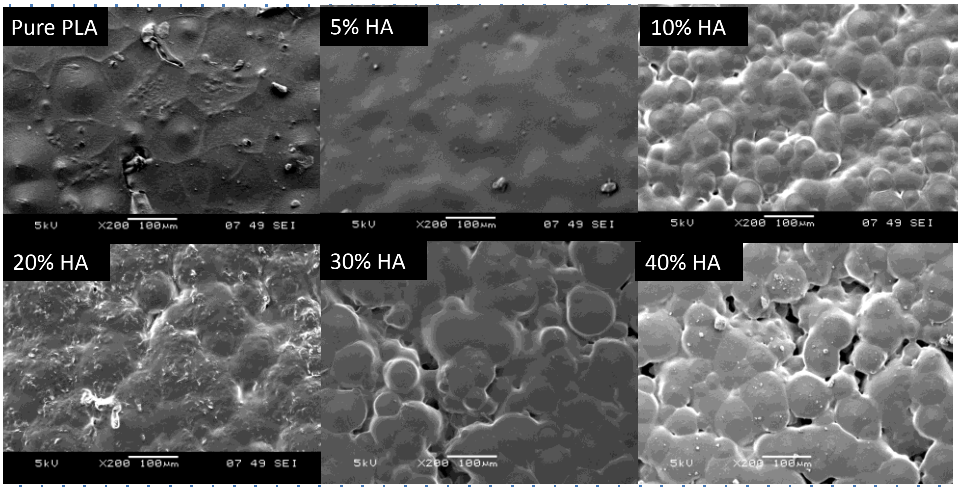


XRD patterns of HA powders



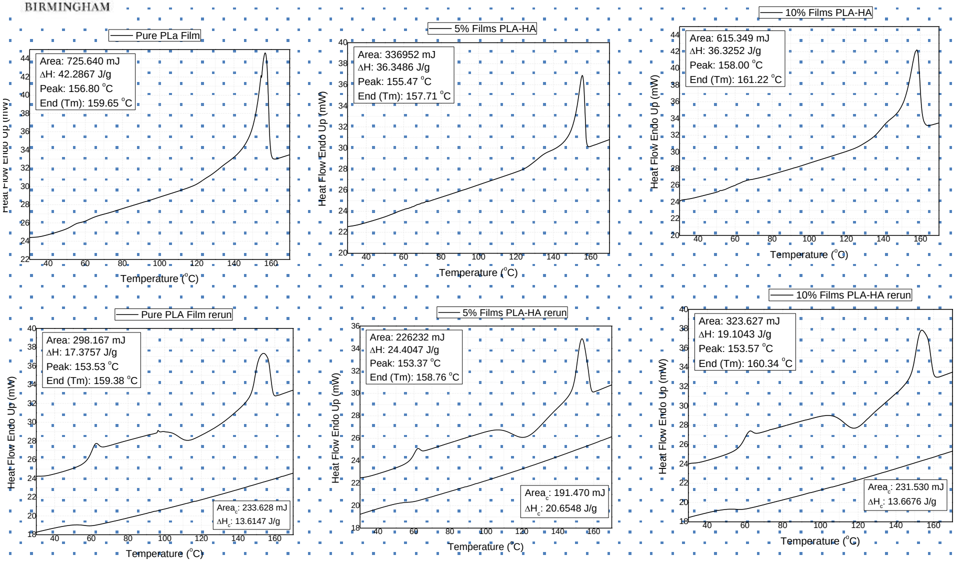
FTIR spectroscopy of HA powders

Results (FDM): Characterization of PLA and HA films : SEM (Different %)



SEM pictures of composite films

Results (FDM): DSC of PLA and HA films



DSC analysis of PLA –HA films

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Results (FDM): DSC of PLA and HA films

HA %	ΔH_f J/g	Peak	Last Trace
0%	42 ±2	156±2	159 ±2
5%	36 ±2	155±2	157±2
10%	36 ±2	158±2	161±2
15%	42 ±2	158±2	162±2

DSC Data from first run

HA %	ΔH_f	Peak	Last Trace	Area T_g	ΔC_p	T_g
0%	17 ±2	153±2	159±2	13±2	0.594	56±2
5%	24 ±2	153±2	158±2	6±2	0.498	57±2
10%	19 ±2	153±2	160±2	11±2	0.422	55±2
15%	25 ±2	155±2	161±2	11±2	0.455	58±2

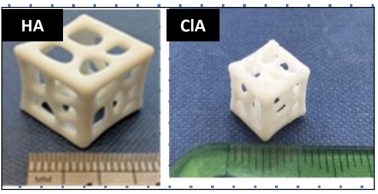
DSC Data from second run

Results (SLA) : 3DP samples

- Rheology studies [1pa.s-8pa.s] are printable

Hydroxyapatite(19µm) and Formlab photopolymer resin		
Solid Loading (HA wt%)	3D printed Sample(green Bodies)	Sintering Process
30%	feasible to be fabricated	Was collapsed
40%	feasible to be fabricated(after three tries)	Was collapsed
50%	feasible to be fabricated(After seven tries)	Was collapsed
60 wt %[34 vol%)	feasible to be fabricated(After ten tries)	Was collapsed
65%	Non-feasible (under investigation)	Not -Applicable

Different solid loading of HA applied in SLA System



SLA 3D printed **HA** and **ClA** samples(30% Solid Loading)

Optimisation point

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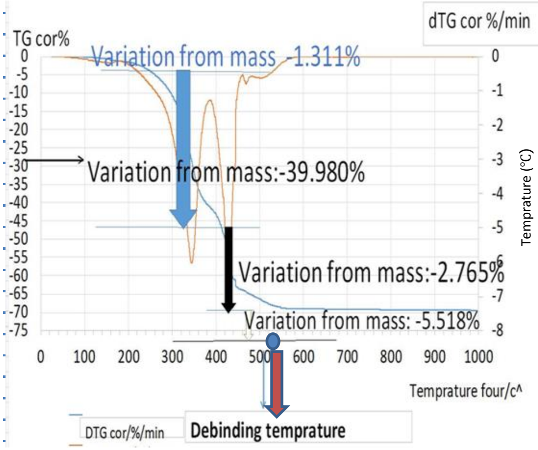
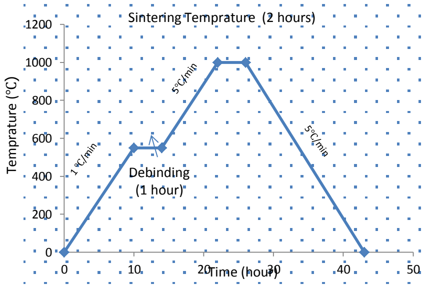
Results (SLA): debinding and Sintering process



TGA of 3D samples



the schematic of **debinding and sintering process**

Scalera, F., et al., *Development and characterization of UV curable epoxy/hydroxyapatite suspensions for stereolithography applied to bone tissue engineering.* Ceramics International, 2014. **40**(10): p. 15455-15462

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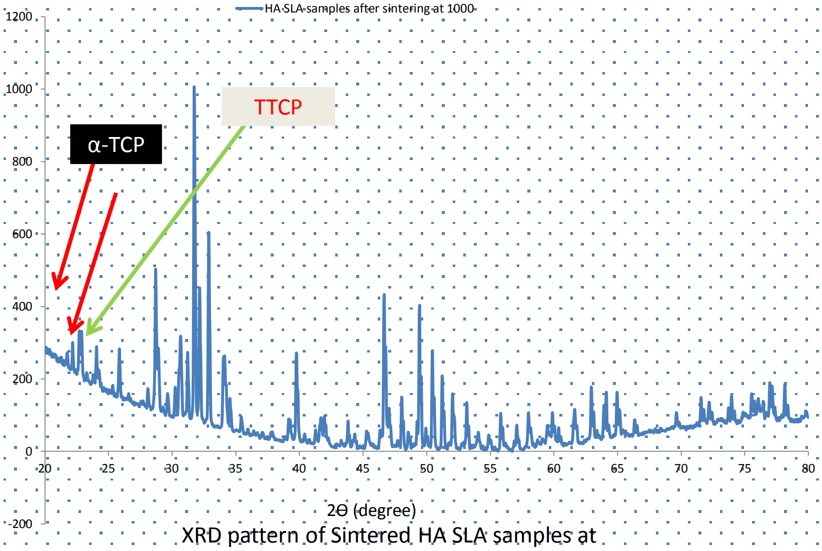
Results and discussion :Sintering -SLA samples



XRD pattern of Sintered HA SLA samples at 1000°C (heat flow 1 degree per minute)

Results (SLM): Flowability measurement

Character	HA (0-30)µm	HA (30-50)µm
Hausner ratio	1.47>1.45	1.24<1.26
Flow character	Very poor	Fair
Time of flowability	No-flowing	2"36
Angle of repose	53.2>46	44.3<45
Flow property	Poor must agitate	Fair-Passable (can be applied)

Results of flowability measurements

Flow Character	Hausner Ratio	Angle of Repose
Excellent	1.00-1.11	25-30
Good	1.12-1.18	31-35
Fair	1.19-1.25	36-40
Passable	1.26-1.34	41-45
Poor	1.35-1.45	46-55
Very poor	1.46-1.59	56-65
Very, very poor	>1.60	>66

Experimental considerations for **Hausner ratio and angle of repose** *European Pharmacopoeia.* International journal of pharmaceutics.

Results (SLM): -HA and ClA(30-50µm)

Parameters:

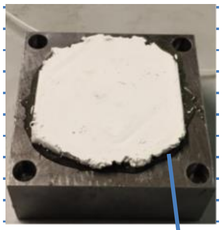
$E_d=P/(s.H)$

Parameter		
Laser power-P (W)	Scanning velocity-S (mm/s)	Hatch distance(H) (mm)
50-60-120-240-400	7000-2000-500-300-100	0.0795

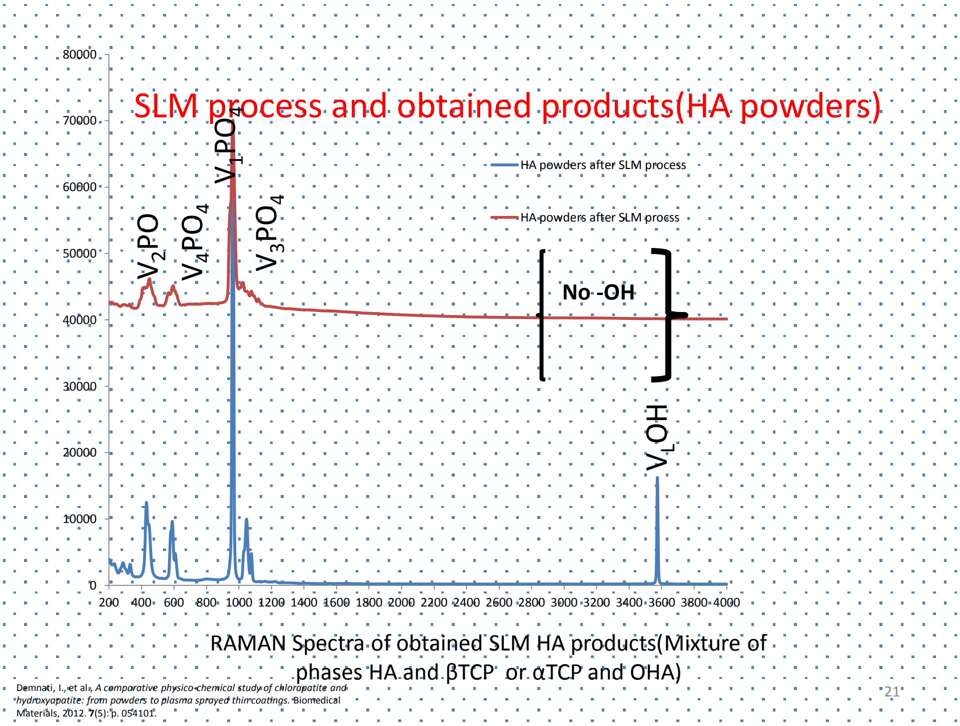
Laser Parameters during the first trial with SLM

- Due to the reflectivity of HA, we could not process over 120 W. 50 W, 100mm/s, 15µm hatch spacing gave a reasonably stable layer in the HA

Support:
On the builds with the aluminium and stainless-steel substrate, the laser mainly interacted with the substrate, decomposing HA powders. However, where we placed a 5mm layer of HA powder on the Alumina substrate, we were able to melt. HA



Support structure from HA **cements** (Thickness:5 mm)



SLM process and obtained products(HA powders)

RAMAN Spectra of obtained SLM HA products(Mixture of phases HA and βTCP or αTCP and OHA)

Demnati, I., et al., *A comparative physico-chemical study of chlorapatite and hydroxyapatite: from powders to plasma sprayed thin coatings.* Biomedical Materials, 2012. **7**(5): p. 054101.

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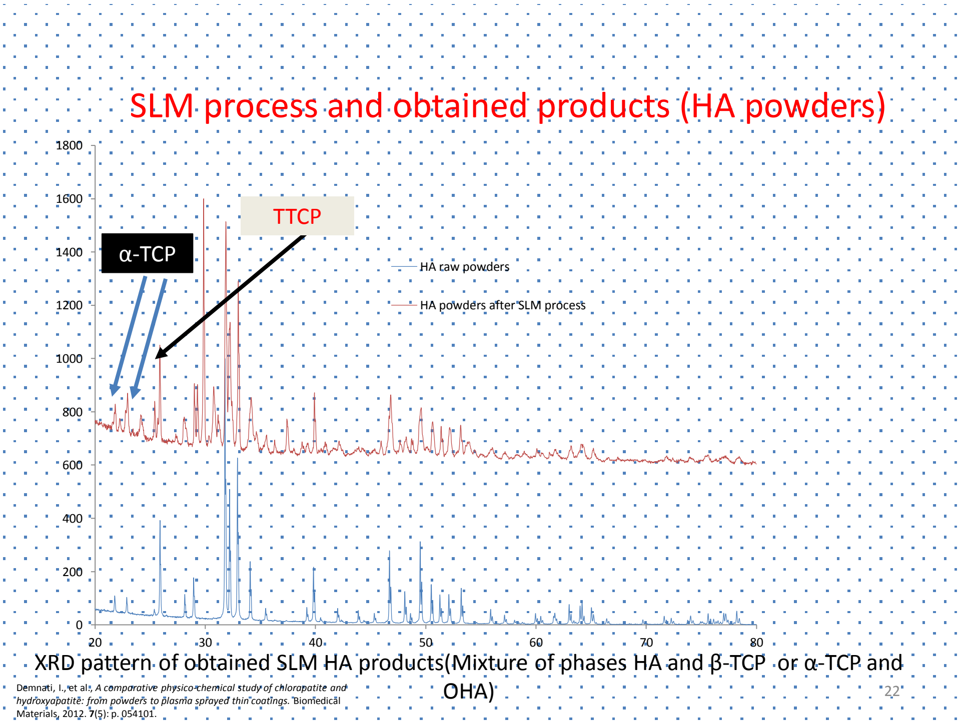

SLM process and obtained products (HA powders)

XRD pattern of obtained SLM HA products(Mixture of phases HA and β-TCP or α-TCP and OHA)

Demnati, I., et al., *A comparative physico-chemical study of chlorapatite and hydroxyapatite: from powders to plasma sprayed thin coatings.* Biomedical Materials, 2012. **7**(5): p. 054101.

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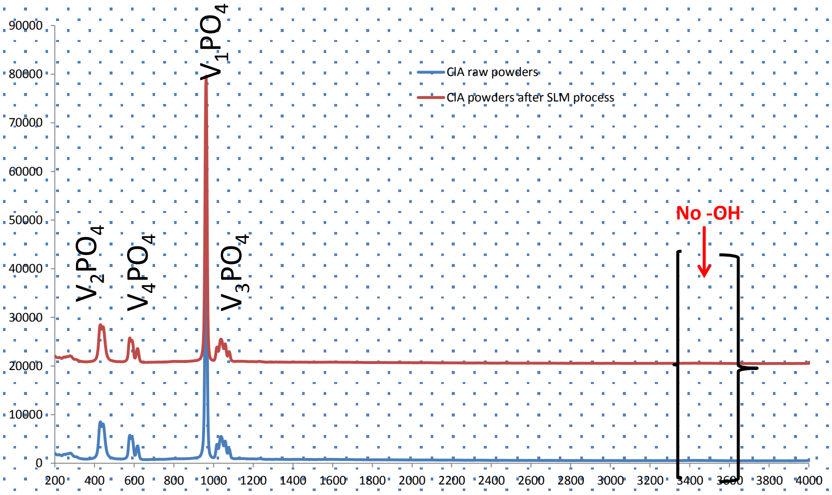
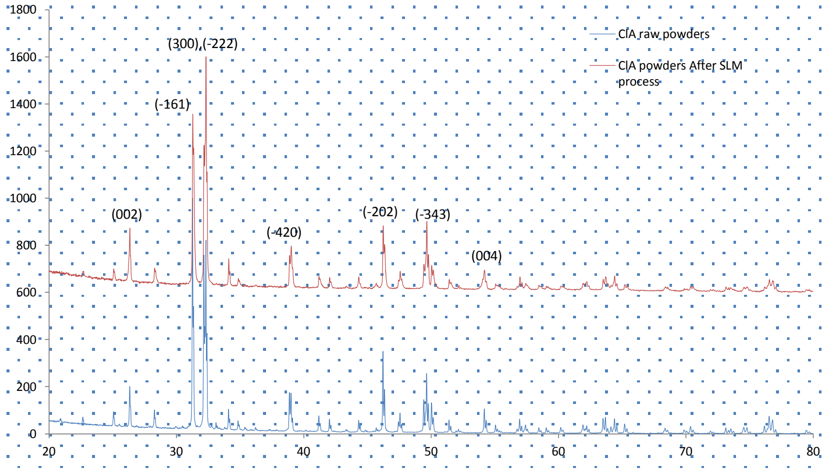
SLM process and obtained products(ClA Powders):



RAMAN Spectrum of achieved SLM products from ClA(Pure ClA-No decomposition)

Demnati, I., et al., *A comparative physico-chemical study of chloroapatite and hydroxyapatite: from powders to plasma sprayed thin coatings.* Biomedical Materials, 2012. **7**(5): p. 054101.

SLM process and obtained products(ClA Powders):



Demnati, I., et al., *A comparative physico-chemical study of chloroapatite and hydroxyapatite: from powders to plasma sprayed thin coatings.* Biomedical Materials, 2012. **7**(5): p. 054101.

XRD pattern of achieved SLM products from ClA-No decomposition (Pure ClA)

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Conclusions

- In FDM process PLA has been fully characterised .HA-PLA films were made by solvent evaporation up to 40% HA as a filler. The composite films were characterised by DSC and SEM to check the thermal history and distribution of filler in the matrix.

- During SLA process the Max solid loading was 60% because of the high viscosity of slurry and the final product was collapsed

- ClA has higher thermal stability than HA, there was no evidence to show the decomposition of ClA to other types of CaP

- In SLM process powders with appropriate flow properties were selected. There was no opportunity to bond and fuse the powders together. The material and the thickness of support are important during the process for ceramics(the same material could be more effective).Also the support should be strong enough to tolerate the high powder laser beam

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Future Work

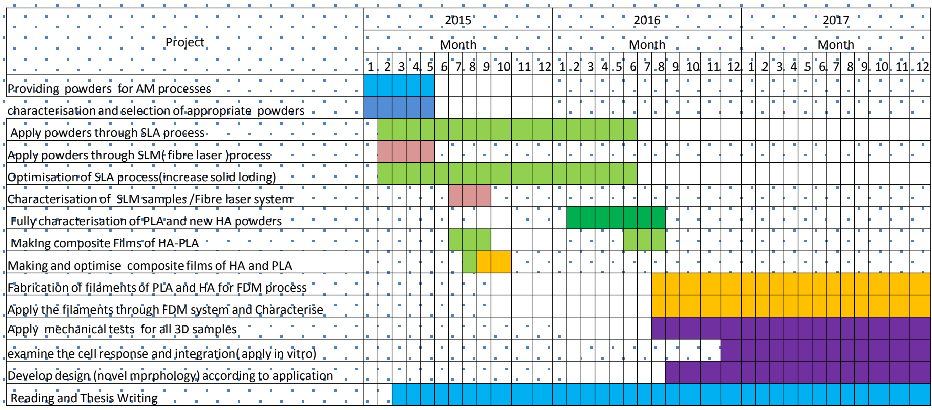
- In **SLA** process Using a two-step debinding process (vacuum and air debinding respectively) to prevent the sample from any defect

- In **FDM** process, 3D shapes of pure PLA , PLA-HA , PLA-HA with different bioglasses will be produced by FDM procedure and the effect of adding the filler to the matrix in terms of degradation ,thermal stability ,Biomechanical performance and cell adhesion will be investigated

- Some films of HA and PLA will be **hot-pressed** and characterised the results will be compared with the 3D printed samples(As reference)

Future Work

Project development schedule

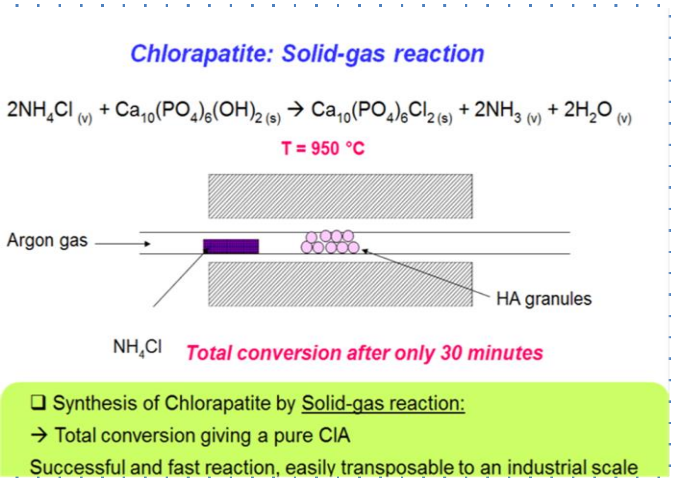


Project	2015												2016												2017											
	Month												Month												Month											
	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3	4	5	6	7	8	9	10	11	12
Providing powders for AM processes	🟦	🟦	🟦	🟦	🟦																															
characterisation and selection of appropriate powders	🟦	🟦	🟦	🟦	🟦																															
Apply powders through SLA process		🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩																		
Apply powders through SLM(fibre laser)process		🟥	🟥	🟥	🟥																															
Optimisation of SLA process(increase solid loding)		🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩																		
Characterisation of SLM samples /Fibre laser system							🟥	🟥	🟥																											
Fully characterisation of PLA and new HA powders														🟩	🟩	🟩	🟩	🟩	🟩	🟩																
Making composite Films of HA-PLA							🟩	🟩	🟩									🟩	🟩	🟩																
Making and optimise composite films of HA and PLA								🟩	🟧	🟧																										
Fabrication of filaments of PLA and HA for FDM process																				🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧
Apply the filaments through FDM system and Characterise																				🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧
Apply mechanical tests for all 3D samples																				🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪
examine the cell response and integration(apply in vitro)																								🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪
Develop design (novel mprphology) according to application																					🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪	🟪
Reading and Thesis Writing			🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦

Thank you

Experimental procedure

HA(commercial powders)



Chlorapatite: Solid-gas reaction

$2NH_4Cl_{(v)} + Ca_{10}(PO_4)_6(OH)_{2\,(s)} \rightarrow Ca_{10}(PO_4)_6Cl_{2\,(s)} + 2NH_{3\,(v)} + 2H_2O_{(v)}$

T = 950 °C

Total conversion after only 30 minutes

☐ Synthesis of Chlorapatite by Solid-gas reaction:

→ Total conversion giving a pure ClA

Successful and fast reaction, easily transposable to an industrial scale

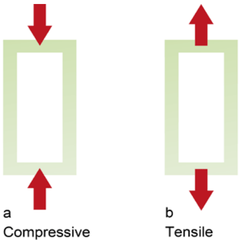
Experimental procedure

Chlorapatite (ClA) was synthesized by a high-temperature ion exchange reaction starting from commercial stoichiometric hydroxyapatites (HA). The ClA powder showed similar characteristics as the original industrial HA powder, and was obtained in the monoclinic form.

The ion exchange reaction was performed in a tubular oven under a flux of dry nitrogen enriched with sublimated NH4Cl in large excess placed in a zone of the tubular oven at about 400°C

Mechanical tests and consideration for human bone:

	Longitudinal direction	Transverse direction
Tensile strength (MPa)	60-70	~50
Compressive strength (MPa)	70-280	~50
Young's Modulus, E (GPa)	11-21	5-13



If the implant is not as stiff as bone, then the remaining bone surrounding the implant will be put under increased stress. If it is stiffer than bone, then a phenomenon known as stress shielding will occur.

http://www.paroc.com/knowhow/mechanical-stability/~/media/Images/Knowhow/Mechanical%20Stability/Illustrations%20EN/Mechanical-properties
3241386.ashx

http://www.doitpoms.ac.uk/tlplib/bones/bone_mechanical.php

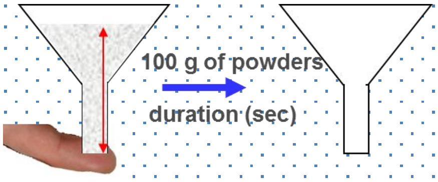
the implant is much stiffer than the bone, then the implant will bear more of the load. Because the bone is shielded from much of the stress being applied to the femur, the body will respond to this by increasing osteoclast activity, causing bone resorption.

Break down bone tissue

Biocompatibility tests and consideration for human bone:

- Protein absorbability study
- Nano-indentation
- Examine cell response and integration-cell adhesion (osteoblasts cells)

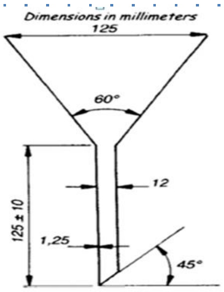
Flowability measurement:



which examines the ability of a powder to flow vertically out of a funnel.

100ml graduated cylinder was used for better accuracy of reading volumes, . The cylinder was filled with a certain mass of deagglomerated powder

The initial volume was measured in three parallels and poured densities calculated. After 10, 250, 500, and 1250 taps the corresponding volume was read to the nearest millilitre



$HR = \rho T / \rho A$

where ρT and ρA are the tapped and apparent density of the powders, respectively.

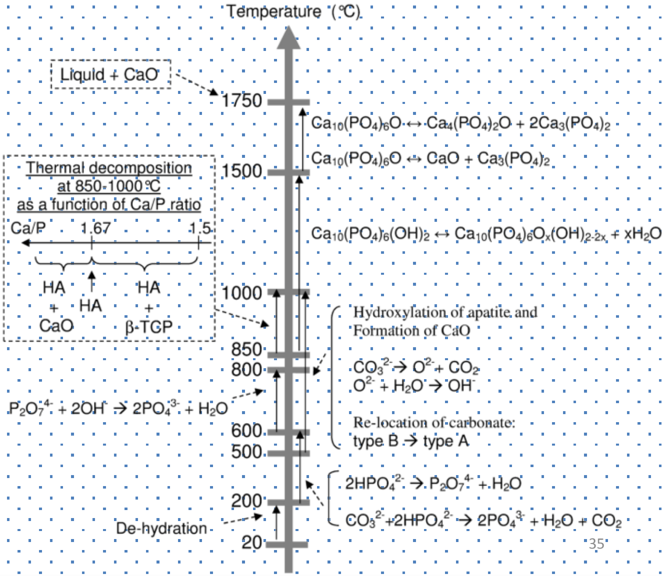
Flowability measurement(tapped density):

The tapped density is obtained by mechanically tapping a graduated measuring cylinder or vessel containing the powder sample. After observing the initial powder volume or mass, the measuring cylinder or vessel is mechanically tapped, and volume or mass readings are taken until little further volume or mass change is observed. The mechanical tapping is achieved by raising the cylinder or vessel and allowing it to drop, under its own mass .

Thermal stability of Hydroxyapatite ?

Decomposition

of HA from T > 900°C



Prostheses and implants materials

hip prothesis

Spinal application

Dental implant

- ☐ Use of bioinert metals to ensure biomechanical fixation
  (Titanium, TA6V, …)
- ☐ Two types of implants response after implantation:
  - Formation of a fibrous soft tissue → clinical failure of implant
  - Direct bone-implant contact → osseointegration(1)

(1) Le Guéhennec L. et al. Dental materials, 23 (2007)

Osseointegration refers to a direct structural and functional connection between ordered, living bone and the surface of a load-carrying implant. Currently, an implant is considered as **osseointegrated** when there is no progressive relative movement between the implant and the bone with which it has direct contact. HA can improve **Osseointegration of metal implants**

A major factor that determines the success of dental implantation is osseointegration, which is the stable anchorage of an implant in living bone achieved by direct bone-to-implant contacts

Major aspects of the implant’s surface characteristics include, but not limited to, surface morphology, surface chemistry, and surface energy, which significantly affect the initial bone cells’ response to the implant at the bone-implant interphase coating, for example, with hydroxyapatite (HA), $Ca_{10}(PO_4)_6(OH)_2$, to improve the implant’s bioactivity. Although the presence of relatively soluble non-apatitic calcium phosphate salts such as ACP, TCP, and TTCP has been found to accelerate the bone attachment, these phases are related to long-term non-uniform coating degradations that adversely affect the prosthetic stability of the implants

Parameter		
Laser power-P (W)	Scanning velocity-S (mm/s)	Hatch distance(H) (mm)
50-60-120-240-400	7000-2000-500-300-100	0.0795

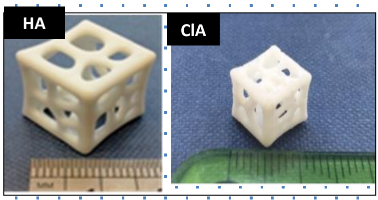
Parameters of SLM
first try

$E_d=P/(s.H)$

Parameter		
Laser power-P (W)	Scanning velocity-S (mm/s)	Hatch distance(H) (mm)
50-60- 100-170-200	50-75-100-150-200	0.15

Parameters of SLM
Second try

Results and discussion :Characterization-SLA 3D Samples (Green Bodies)

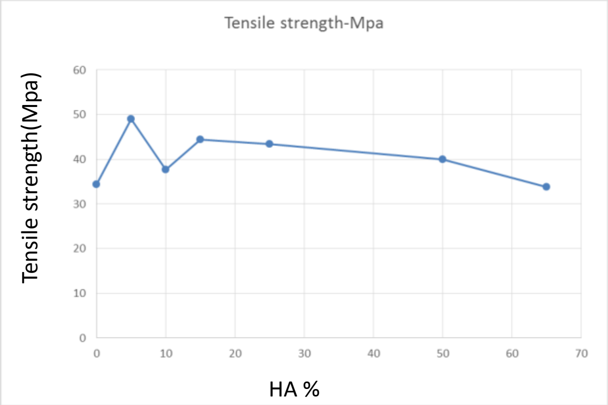


SLA 3D printed **HA** and **CIA** samples(30% Solid Loading)

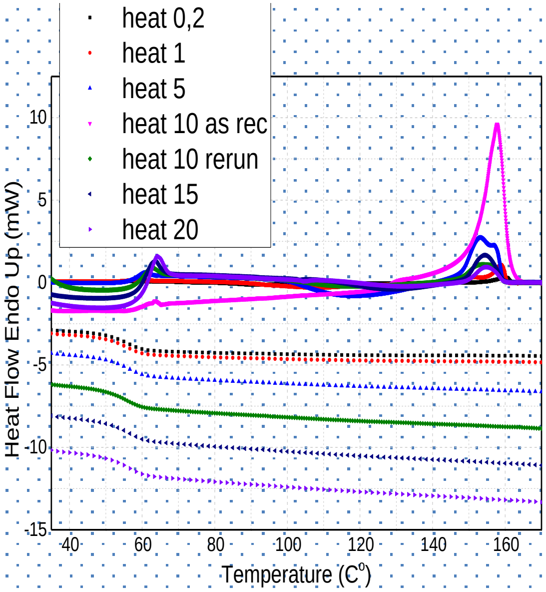
Hydroxyapatite(26µm) and Formlab photopolymer resin		
Solid Loading (HA %)	3D printed Sample(green Bodies)	Sintering Process
30%	feasible to be fabricated	Was collapsed
40%	feasible to be fabricated(after three tries)	Was collapsed
50%	feasible to be fabricated(After seven tries)	Was collapsed
60%	Non-feasible (under investigation)	Not - Applicable

Different solid loading of HA applied in SLA System

PLA and HA Films Extrusion Tensile Strength test



Results and discussion: DSC-constant cooling rate 10 deg/min -Play with heating rate

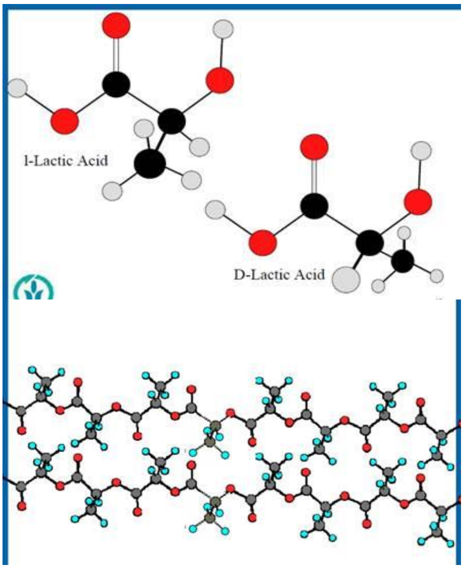


Chapters of Thesis

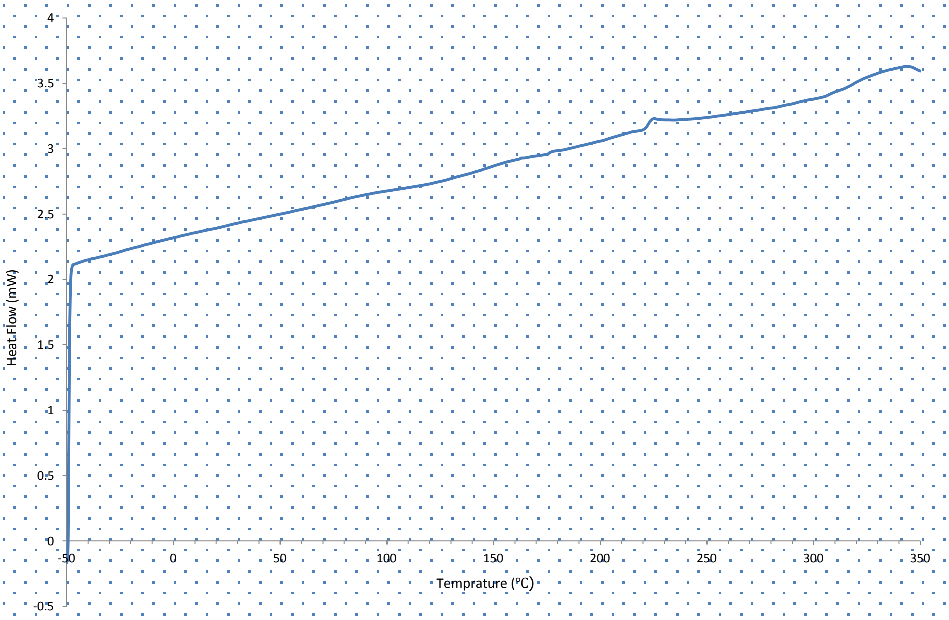
- Chapter 1: Literature review
  1. Bone and scaffold
  2. Different Biomaterials which could be used
  3. Conventional methods of making scaffold
  4. 3D printing
- Chapter 2: Fully characterisation and mechanical tests PLA-PLA-HA composite Films)-Hot pressed samples
- Chapter 3: Fully characterisation and mechanical tests of 3D printed PLA-HA samples
- Chapter 4:Fully characterisation and mechanical tests of 3D printed lanthanum glasses-HA PLA or another filler(Novelty)
- Chapter 5:SLM-SLA
- Chapter 6:comparison –conclusion-Future work

Questions

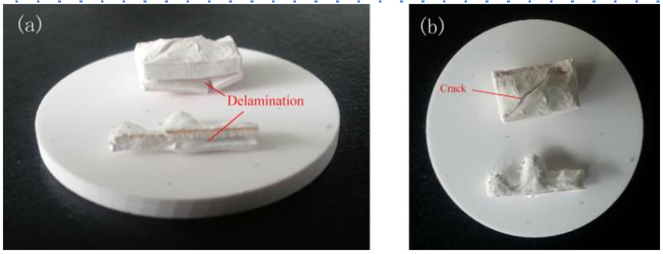
- What is the point of HA to TCP and other calcium phosphates and biomaterials which can be used as bone implants?

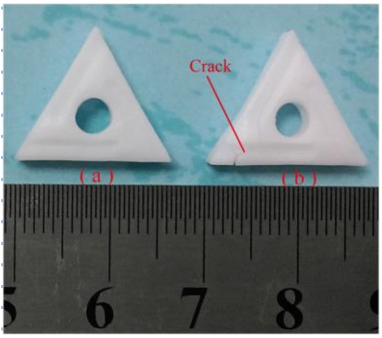


PLA is a stereoisomer
D content into 3052D is about 3-4%



Debinding on Air





The sintered body obtained from(a)a two-s tep profile debinding; (b) vacuum debinding

- The sample that is debound in air exhibits a large number of defects, as shown in Fig. 6, which is attributed to the very high pyrolysis rate of the organic compound. The gas generated during the pyrolysis cannot escape from the body in time. Thus, a partial pressure is generated inside the body, re- sulting in the formation of defects
-

Next, vacuum debinding was employed to control the pyrolysis

because the pyrolysis rate is much lower in a vacuum environ- ment. The gas generated during the vacuum pyrolysis process can escape more easily from the channels between the particles in the body. However, the residual carbon in the debound body would produce gas during the following sintering process, leading to the formation of cracks in the body during sintering, as shown in Fig. 7(b).

Therefore, a two-step debinding process was adopted to protect the sample from having any defects.

. The first stepofthedebinding processwastheaforementionedvacuumdebinding.Then,asa second step,anairdebindingprocesswasapplied,asshownin Fig. 2(b).

UNIVERSITY OF BIRMINGHAM

Results and discussion: Hot-Stage-isotheraml 120degrees from melt