Reporting Our Progress on

Selective Laser Sintering for sustainable polymers

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Contents

01
Introduction to AM

- Polymers in AM
- Common AM techniques
- FDM
- SLS

02
Available Materials

- PHA
- PBS
- PBAT

03
Powder production

- Requirements
- Mechanical Milling
- Chemical Precipitation

04
Future developments

- Environmental impact
- Thermal rounding

Part 1:

Introduction to AM

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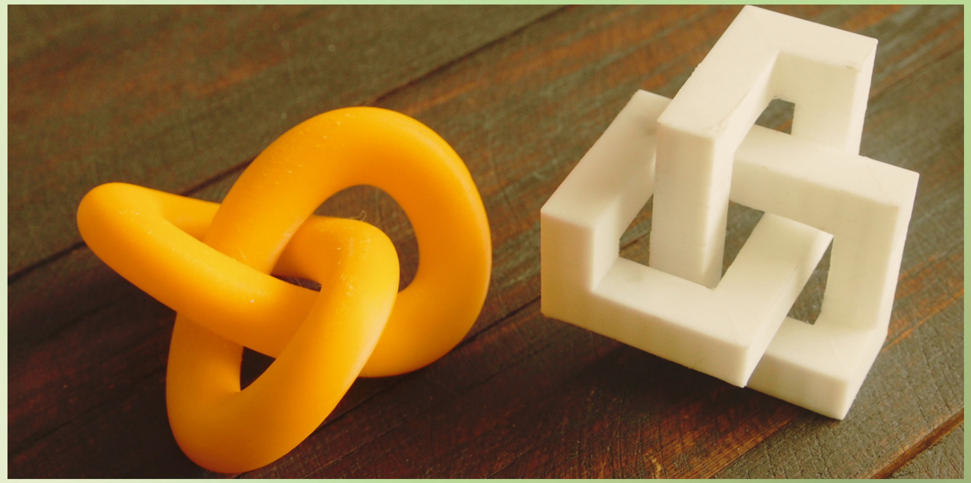
May 12, 2022

Additive Manufacturing

Complex geometries



Minimal waste

Simplified design pipeline

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Date:
May 12, 2022

Polymers in AM

Polymers and their composite materials have been used in all sorts of fields,
ranging from arts and crafts all the way to advanced biomedical and aerospace applications, thanks to their unique and varied extended range of properties.

The rapid advancement of AM, where polymers have been extensively used for
prototyping, in the form of *resins, filaments, powders and viscous inks*, has increased the demand for high-performance polymers, in order to take advantage of their quicker printing times (compared to metals) as well as their lower cost, while still maintaining good mechanical properties for an end product, rather than just a prototype

AM Techniques

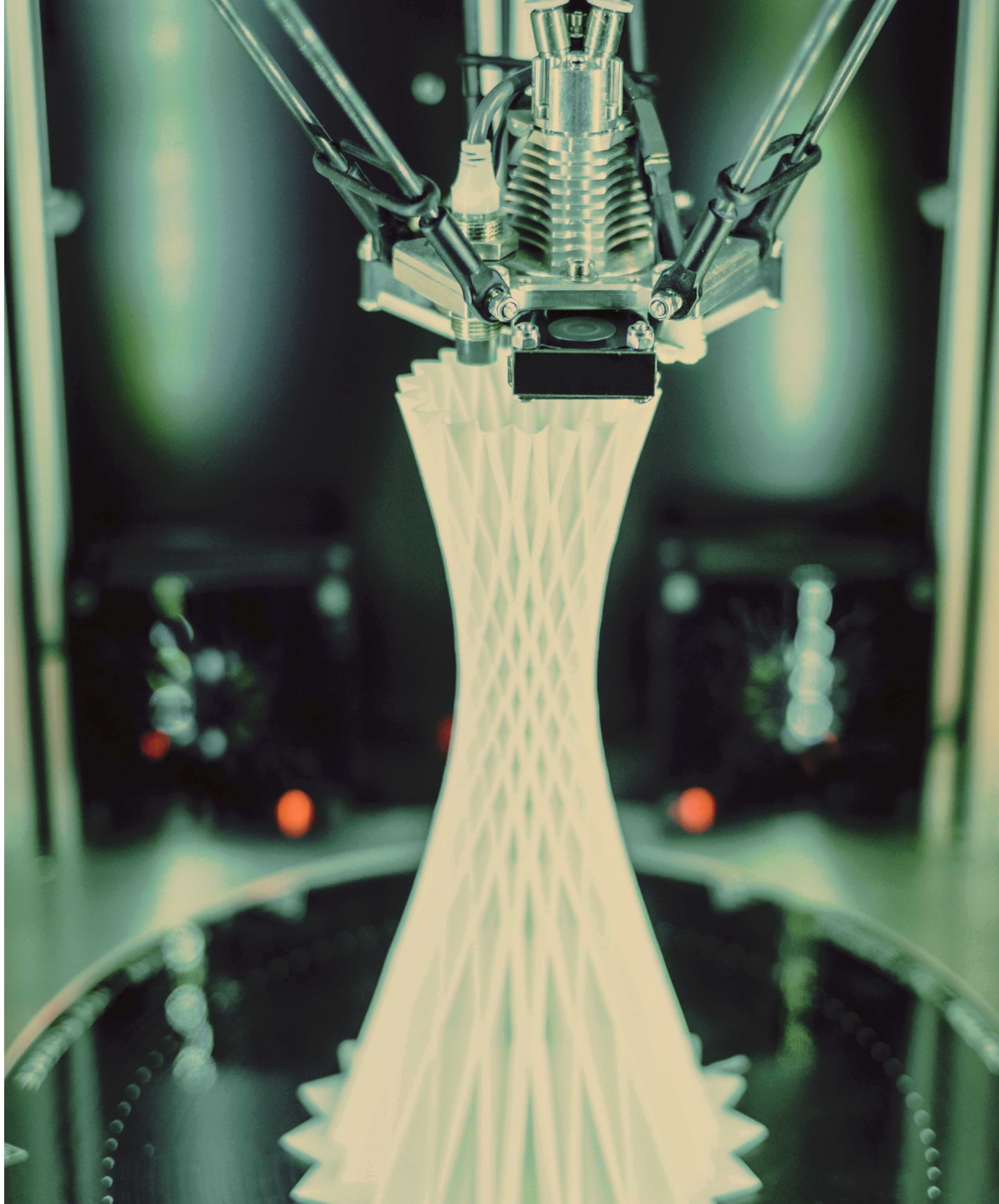
- *VP (Vat Photopolymerization)*, which makes use of UV lights to solidify photosensitive resins. This class of AM processes can produce parts with the highest resolution among all AM methods

- *MJ (Material Jetting)*, which consist of a deposition of viscous fluids (either in droplets or in a continuous fashion), solidified by different agents

- ***PBF (Powder Bed Fusion)***, where the object is printed by locally fusing a powder bed (with a pulsing energy source, such as lasers or with an electron beam), layed out in a layer-by-layer fashion

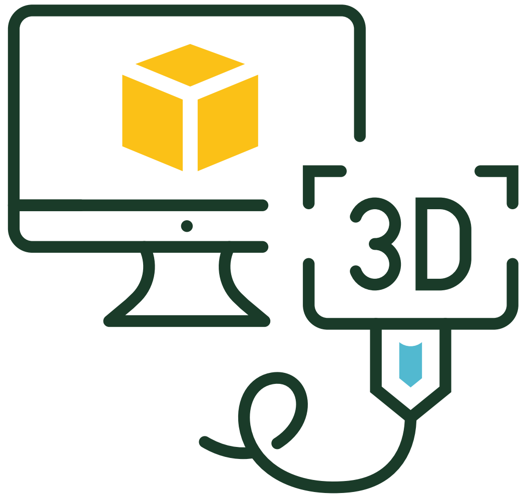
- ***ME (Material Extrusion)***, where each layer is printed by direct deposition of materials through a nozzle, that solidify as they cool down

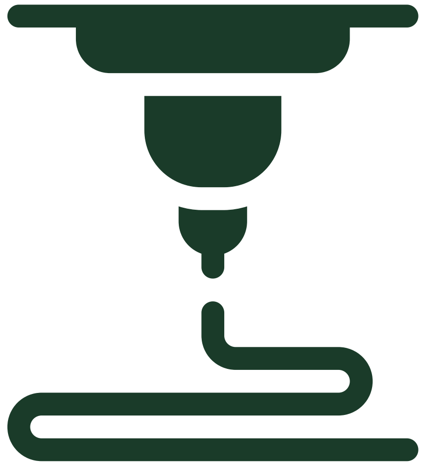
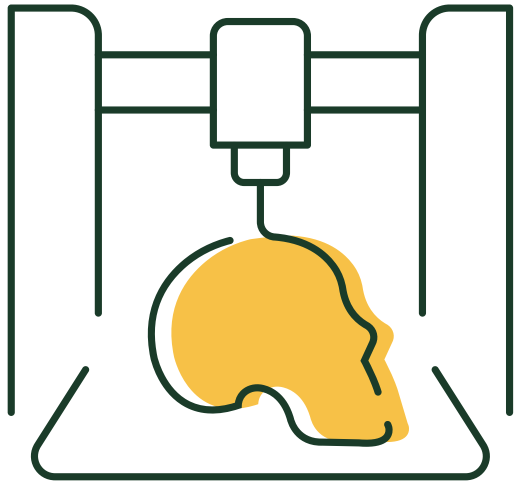
- *Sheet Lamination*, where thin sheets of material are stacked together and bonded with adhesives or heat. This class of techniques is not entirely additive, since subtractive processes are used to cut and refine the final part, creating substantial material waste



Fused Deposition Modeling

- Most well known technique
- Layer by layer deposition of a filament
- Accessible and cost effective
- Usable with a wide variety of materials (PLA, ABS, PET, PETG, HIPS, TPU, nylon, etc)
- Decent quality, fast prints
- Slicing software optimized for this method

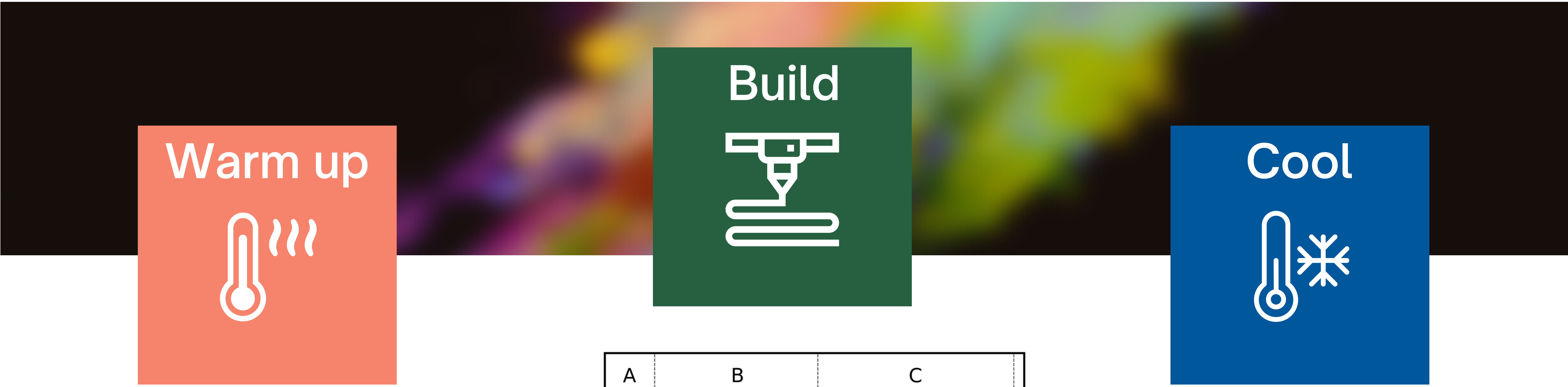


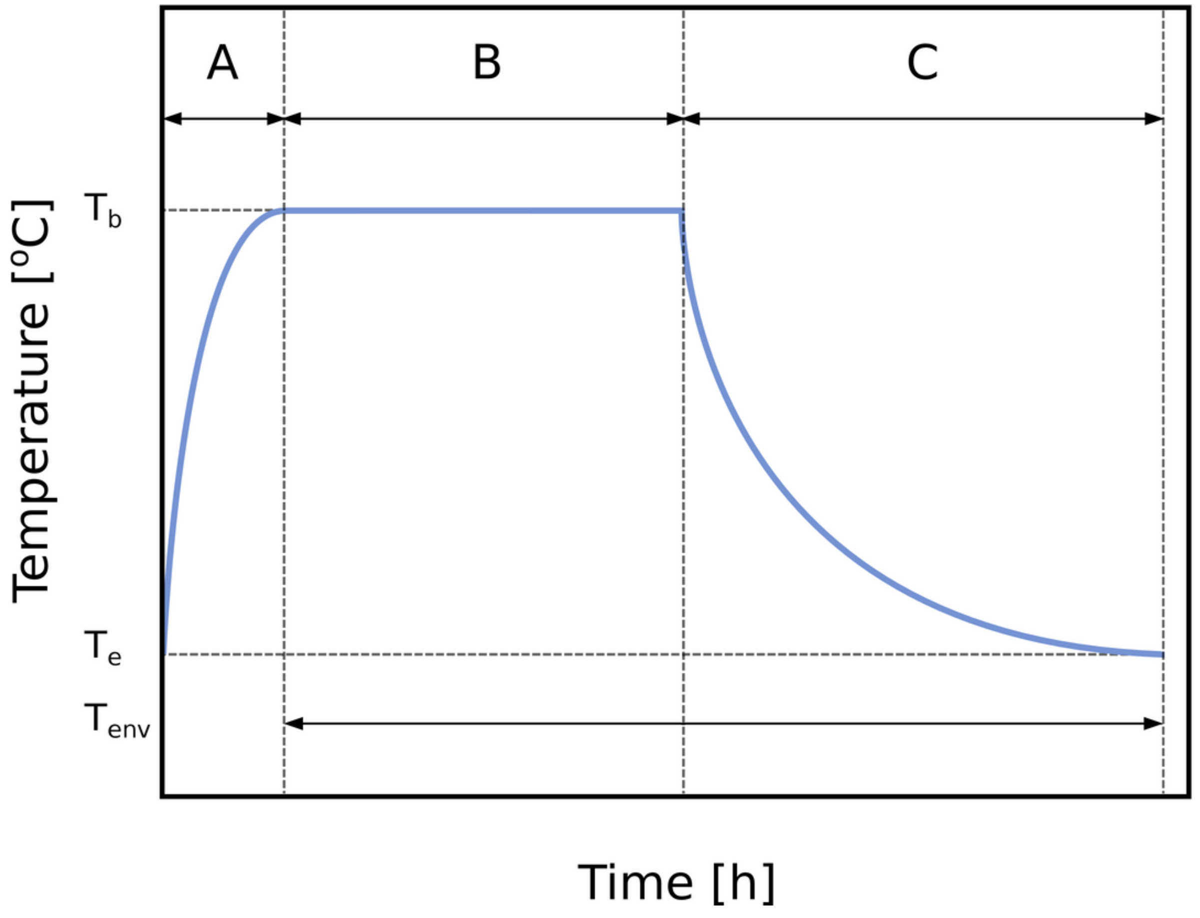




Selective Laser Sintering

SLS is a manufacturing process in the PBF family.
A powder bed is layed out onto a platform and a focused heat source (a laser) locally sinters the powder, until a single layer is completed.
A mechanism wipes out the remaining powder, which is recollected and automatically redistributed by a recoating system, for each subsequent layer.

Triple stage process





Part 2:

Available Materials

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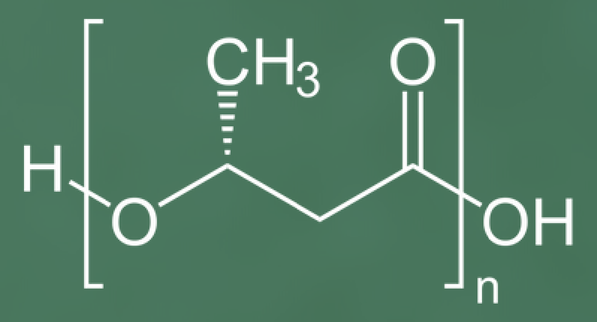
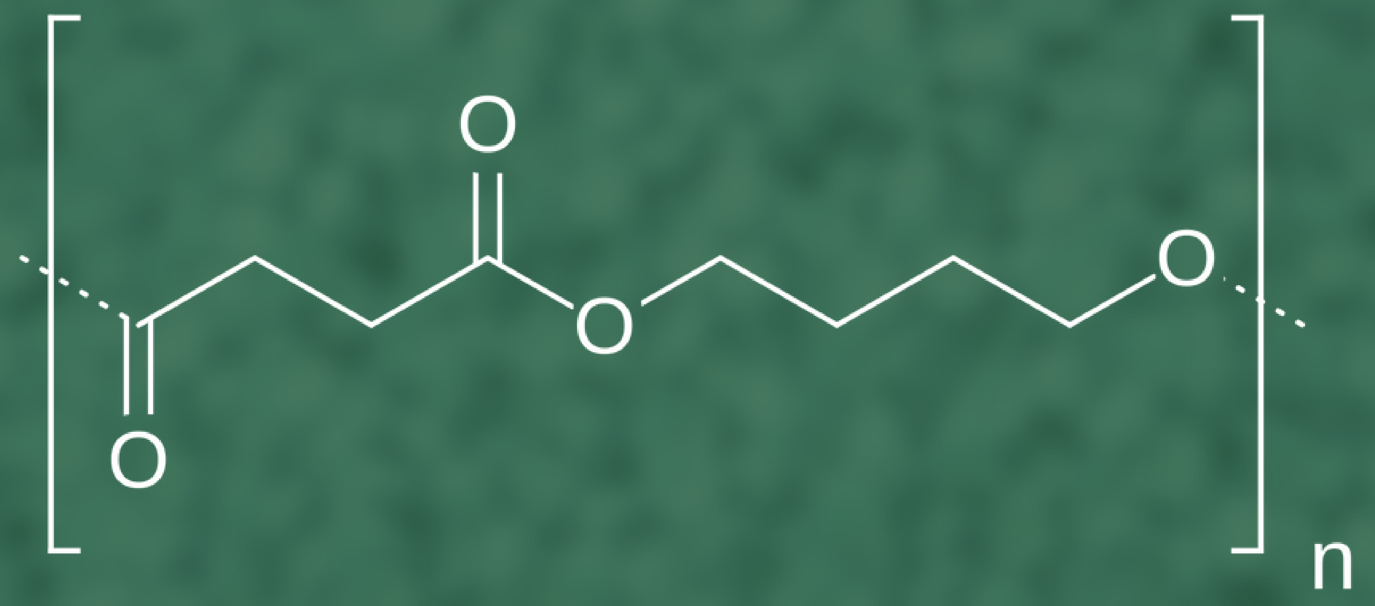


PHA (Polyhydroxyalkanoates)

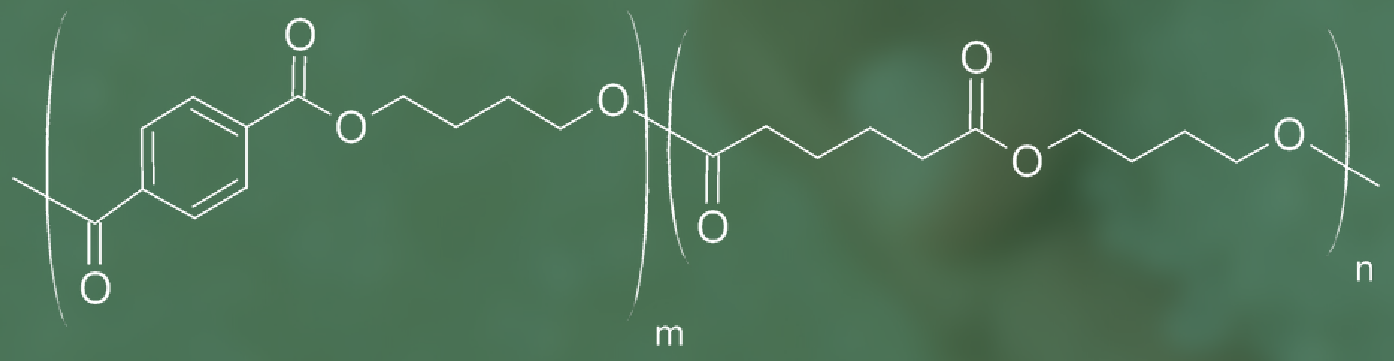
PHAs are a family of thermoplastic polyesters, obtained by hydroxyalkanoic acids via bacterial fermentation, under nutrient depletion and carbon excess conditions.

PHBH *Poly(3-hydroxybutirate-co-3-hydroxyhexanoate)* is a copolymer of the PHA family, which gained interest in the AM field and specifically in SLS applications, since it has a wider sintering window than other polyhydroxyalkanoates



PBS (Polybutylene Succinate)

PBS is an eco-friendly biopolymer, which rose interest among industrial and academic environments.
While generally brittle, relatively expensive and still challenging to manufacture in SLS-ready powders, this polymer has very desirable features, such as high processability, flexibility, as well as visual clarity and specularity



PBAT (Polybutylene Adipate Terephtalate)

PBAT is one of the most promising biopolymers in the sustainable plastics market, since it is very eco-friendly and, at the same time, more performant than comparable alternatives such as PHAs, which exhibit poor mechanical and thermal properties, whereas PBAT is closer to higher performance petro-chemical polymers such as polyethylene terephtalate (PET) and polybutylene terephtalate (PBT)

Part 3:

Powder Production

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May 12, 2022

Powder requirements

Size distribution

Ideally, a gaussian distribution, with most particles close to the average size is desirable, with a tipical range of (20 ÷ 80) μm.
The average particle size directly influences the layer thickness in the SLS process.

Morphology

Particle morphology is crucial in the sintering mechanism, where regular, smooth and non-hollow spherical geometries are preferrable

Sintering window

SLS is characterized by an optimal sintering window, between crystallization (Tc) and melting (Tm), in which the material is in a metastable phase, where full coalescence of the top powder layer, as well as adhesion with previously sintered layers are most likely guaranteed

Mechanical Milling

Grinding plastics into fine and homogeneous powders can be a challenge, since the high speed milling devices can easily *overheat the plastics* above their softening point, creating lumps of material, far from the desired result.
A solution to this problem is using so called **cryogenic grinding** devices, which utilize cooling agents such as dry ice, liquid carbon dioxide or *liquid nitrogen*, in order to keep the plastics below the glass transition point, where polymers become intrinsically brittle, similarly to a ceramic material, making it possible to turn the original mass into a powder.
Despite being an effective process for powder production, the **morphology** obtained with cryogenic milling is extremely *irregular and unpredictable*, which makes this method generally unsuitable for high quality SLS parts

7
N
Nitrogen

Chemical Precipitation

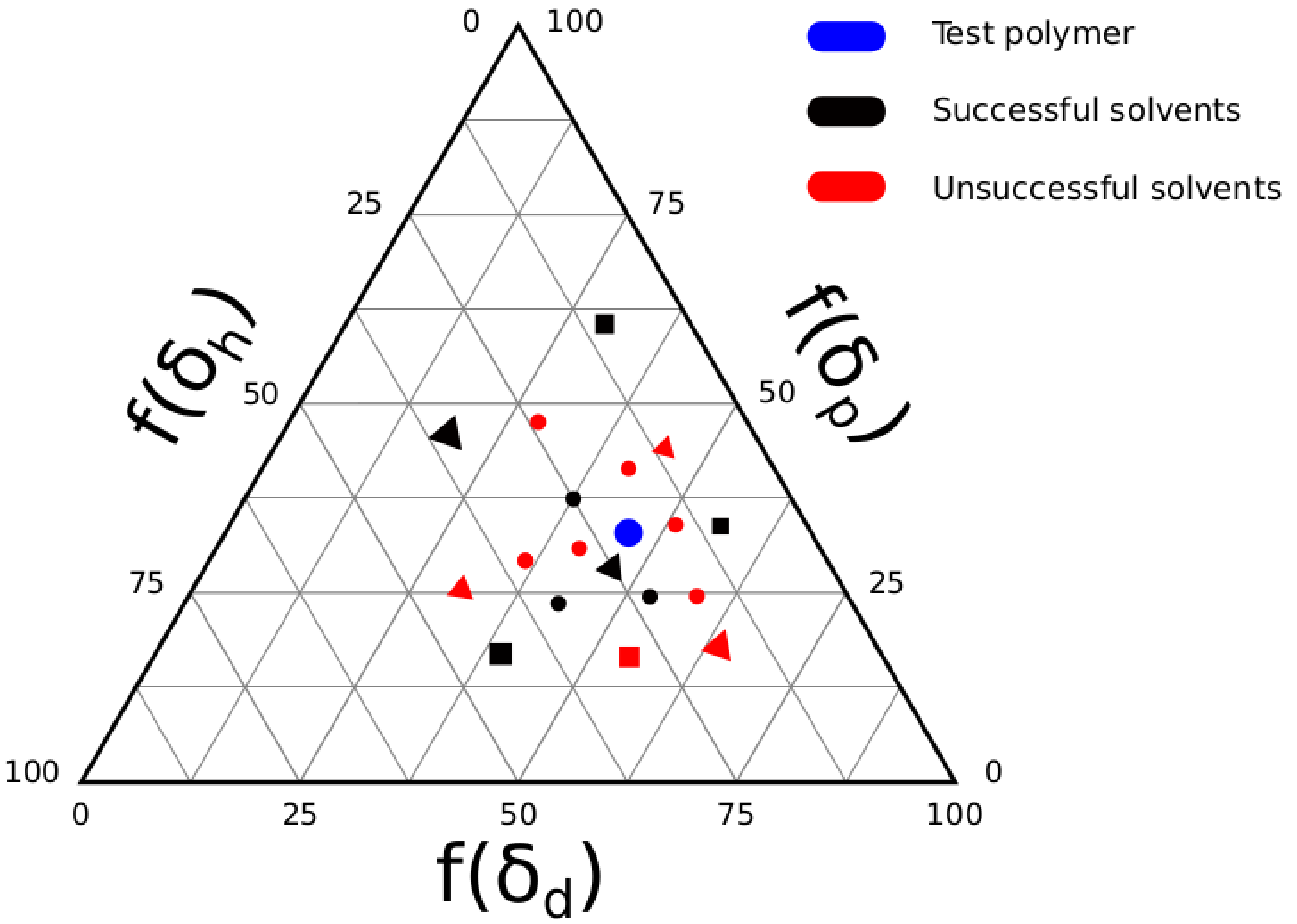
Many polymer powders can be produced using the precipitation method, but their development is currently very limited and in early-stage, especially with thermoplastics.
The recommended solvent choice gravitates towards so called **moderate solvents**.
These compounds have the peculiarity of acting as a solvent only when heated above a certain temperature. Therefore, thermoplastics can be dissolved into a compatible solvent and form a liquid-liquid *phase separation upon cooling* of the system, where complex crystallization and **precipitation** phenomena are later induced via **stirring** of the nucleated polymer-rich droplets.

Solvents are pre-selected using the **Hansen** parameter equation

$$f(\delta_x) = 100 \cdot \frac{\delta_x}{\delta_d + \delta_p + \delta_h}$$

which quantifies the polymer-solvent interaction,

The interaction is better visualized in a **TEAS** plot.



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May 12, 2022

Part 4:

Future developments

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May 12, 2022

Environmental Impact

At first glance, **cryogenic milling** seems to be a **more sustainable** option for powder production. However, this method is currently **unsuitable for SLS**, unless future development will improve overall powder morphology.

On the other hand, while powder production by **chemical precipitation** produces much better and more controllable powder feedstock, it is worth noting that organic solvents are intrinsically **environmentally impactful** and that should be taken into account, especially for large scale production of these powders.

The **entire purpose** of utilizing sustainable biopolymers in the first place might be rendered pointless, if their powder production utilizes compounds or processes that are not **environmentally friendly**.

Better innovative solutions (or mitigations of the mentioned issues in the current pipelines) need to be implemented in the near future.

Thermal rounding

Thermal rounding is a **heat treatment**, aimed at improving the bulk powder morphology for SLS applications.

This kind of treatment might be the crucial step in the success of a more environmentally friendly pipeline, which does not involve any polluting solvent.

Powders can be heated either **directly**, with a carrier gas, or **indirectly**, using heated walls.

While the former method has a better process **yield** and reduced risk of lumping, the latter produces powders with a better, more **spherical morphology**, but with a significantly higher risk of particle agglomeration.