MASTER THESIS

Sustainable FDM printing using eggshells

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Client: Reflow
Company Mentor: Jasper Middendorp

April 2022

COLOPHON

Master Thesis
Sustainable 3D printing using eggshells
MSc. Integrated Product Design

April 12, 2022
Faculty of Industrial Design Engineering
Delft University of Technology
The Netherlands

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Acknowledgements

I would also like to take this opportunity to all that have supported my in this project and helped me in deal with all the challenges that the project has brought:

First of all I would like to thank the supervisory team, consisting of dr. Jeremy Faludi and dr. Sepideh Ghodrat. Dr. Jeremy Faludi has incredible knowledge about sustainability of additive manufacturing and lots of experience in printing with paste and with his help I've been able to make some great breakthroughs in improving both material recipes and printer. Dr. Sepideh Ghodrat has helped me a lot in dealing with all the struggles and challenges, both technical and motivational. She has always been able to motivate me and explore new directions.

I would like to thank Jasper Middendorp and his company, Reflow, for taking on this challenge with me. His enthusiasm for making additive manufacturing has been very inspiring and he has kindly provided the printer and other hardware needed for the project.

I would like to thank Israel Carrete, who has helped me in analysing some of the printing results in order to further improve them and who helped me in doing the bending test.

I would like to thank Constantijn Crijnen, whose printer modification design has been a great inspiration for the modification I made myself and his help in solving some of the issues that I ran into with the printer has made it possible to make the printer work as well as it does.

I would like to thank Atula Jadhav, who thought with me in solving some of the printing issues that I ran into and spend way too much time coming up with solutions, while she was also working full-time on her own graduation project.

I would like to thank Queen Leung, for helping me deal with my stress and helping me to rest well and relax during the weekends in order to charge my batteries for the next week, as well as arranging two wonderful holidays for us to go on together in order to clear my head.

I would like to thank my friends and family who've supported me through all the ups and downs of the project by being there for me when I was struggling and celebrating with me when things went well. And I'm also thankful for their willingness to help collecting eggshells for me.

And lastly I would like to thank everyone that I've met and spoke to in the lab. There have been many conversations with fellow students and members of staff that have sparked inspiration for new tests and new modifications. It was always a pleasure to discuss the projects that everyone was working on.

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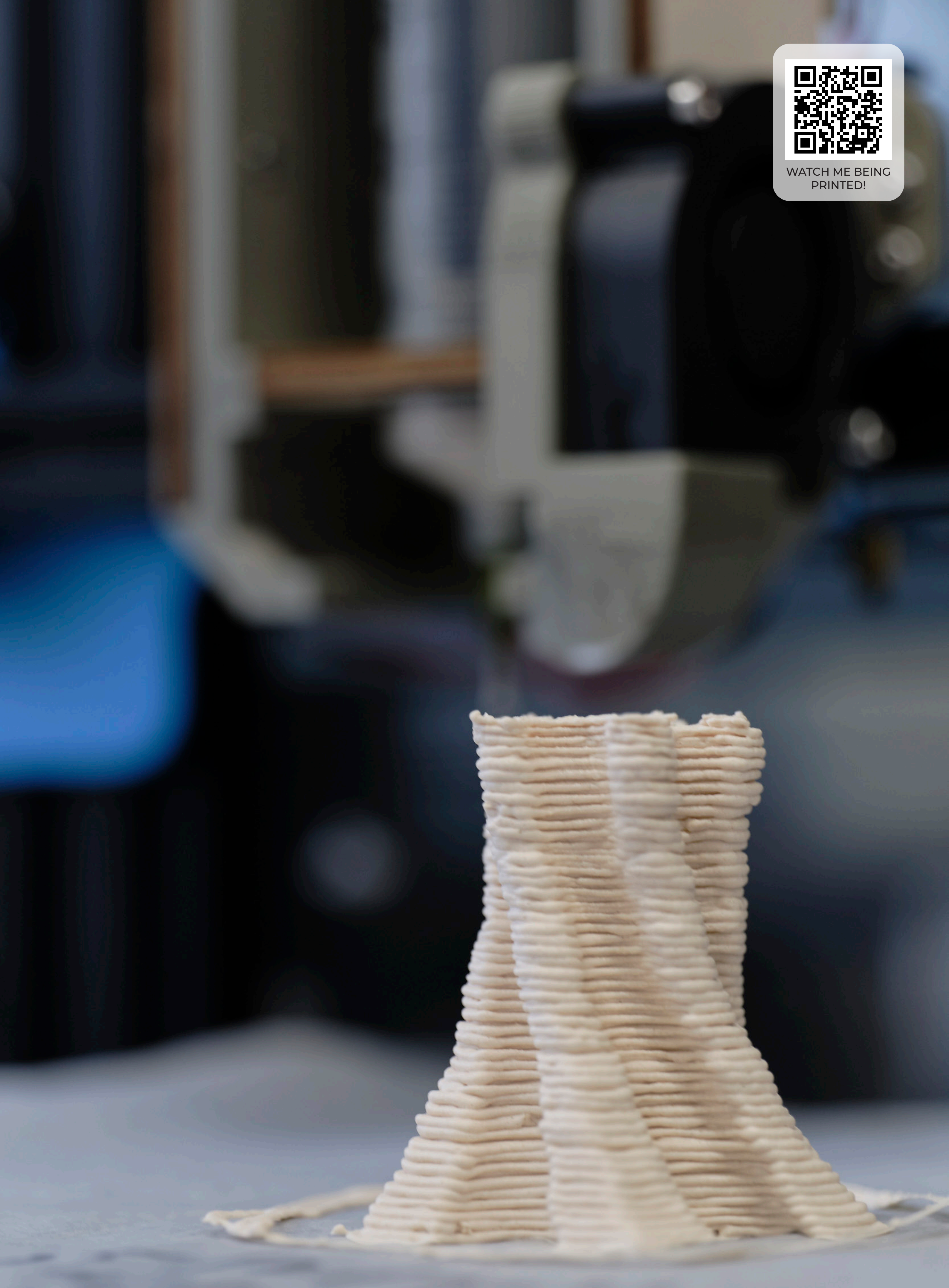

WATCH ME BEING PRINTED!

Figure 2: Vase print using final material mix recipe

Ch. 1 | Introduction

This chapter serves as an introduction to the project and explains the backstory and motivation behind it. The project has a lot of facets and a clear understanding of the motivation of the project is needed in order to follow the steps and procedures that have been taken in working towards the end result.

Introduction

Additive Manufacturing (AM), more commonly know as 3D-printing, is a relatively new group of production methodologies that have been evolving rapidly over the last couple of years. The most well-know AM methodologies, Fused Deposition Modeling (FDM) and Fused Filament Fabrication (FFF), have gained a lot of popularity over the last few years with dozens of companies developing printers and already hunderds of options available to buy. FDM printing has become more than affordable than ever with printers being available for as little as 150 euros. These printers have become a go-to for designers, architects, artists and hobbyists, allowing them to make quick prototypes, display models, artwork and replacement parts for household items. Whereas making a part or prototype with traditional methodologies can take several days, weeks or even months, making one with FDM/FFF can be done in just a few hours.

Problem Definition

While FDM printing is being lauded for it's ability to quickly produce complex geometries, not much light is shed on the environmental impact of the technology. The Specific Energy Consumption of FDM is rather high when compared to other production techniques as the printed material has to be heated to its melting point throughout the printing process and the materials themselves are not sustainable either. Often virgin plastics are used as filaments for FDM that find their origin in valuable resources such as food and oil.

In other words, although the possibilities of FDM are incredible, from an environmental sustainability standpoint, the methodology is far from perfect. This is an issue that should be addressed.

There is a need for materials that are suitable for FDM printing, are less detrimental for the environment and fit in a circular economy.

Research Objectives

Goal 1:

The first goal of this research is to develop material mix recipes that:

1. Are suitable for FDM printing
2. Are less detrimental for the environment than the commonly used plastic filaments
3. Could serve as an alternative to the commonly used plastic filaments.

Each of these requirements for the to be developed material mixes come with their own requirements and wishes.

Suitability for FDM printing

Suitability for FDM printing will be determined by the material mix's

1. Printability; the ability to extrude & self-support, including starting & stopping cleanly, as well as printing time
2. Dimensional accuracy; no shrinking or warping, matching CAD model dimensions
3. Resolution; primarily layer height, so resolution in Z-direction
4. Surface finish; smooth and uniform surfaces, not rough or broken

5. Price; material cost per kg

Lowering environmental impact

Lowering the environmental impact of FDM can be achieved by:

1. Creating a material mix that can be printed at room temperature, eliminating the need to heat up neither hot end, nor printbed.
2. Having the material mix fit in a circular economy, where the material mix is degradable and/or can be reused, and ideally a material mix whose components are derived from waste streams rather than being valuable resources in their own rights.

Replaceability

Material mixes' ability to serve as a replacement or alternative to the commonly used plastics partially depends on the factors that will be assessed under their suitability for FDM printing, but also extends to their mechanical properties. Mechanical properties will NOT be tested in this project, but it is important to mention them as it is unlikely to expect that many FDM users will opt for the use of these paste-like materials if they don't approach, match or surpass

In order to built a frame of reference for the found material mixes, the found material mixes will be compared to filaments made by Reflow, the client of this project. Reflow manufactures filaments made from recycled plastics. The two filaments that will be used as reference materials are rPLA and rPETG, which are made from recycled PLA and recycled PETG respectively. rPLA is made from recycled food packaging, whereas rPETG is made from recycled serving trays obtained from hospitals.

Goal 2:

The second goal of the project is strongly related to the first goal, and is to develop a printer modification that is capable of printing with paste-like material mixes, while being simple enough to be used in house-hold contexts. The printhead design that is used for most FDM printers are based on the idea of a wire-like filament that runs into the printhead where it melted and deposited through a nozzle. This setup is not suitable for printing with paste-like materials and thus, a modification will need to developed.

Goal 3:

The third goal of the project is to develop a set of guidelines for testing and printing with paste-like material mixes. As paste-like materials are likely to respond differently than plastic filaments, it will be necessary to find out what slicing/print settings have most impact on the printresult and finetune these settings in order to have the best print results possible with the material mixes that are being tested. Impacts of the various slicing settings will be analysed in order to gain an understanding that will allow fast improvements to gotten printresults.

Methodology

The project follows een iterative design cycle in which material mix, print settings and printer modification are altered based on their respective performance and impact on the results.

Material Mixes

In the search for material mixes that are suitable for FDM printing, various materials will be tested. In testing different material combinations, impacts of the various ingredients will be analysed and ratios will be adjusted in an interative manner in order to find the best material mix possible.

Print Settings

The effect of various print settings on the printing results will be analysed in order to optimise the settings for each material recipe and each 3D model. This will be done in an iterative process where settings will be changed one by one, while other parameters (settings and used material mix) will remain fixed. This way impact of each individual setting can be identified so it can be applied to the project's advantage.

Printer Modification

For the development of a printer modification, currently available designs for paste-printers will be reverse engineered in order to better understand their working principle and select which one works best for the goal of this project. Based on the design, a new version will be developed that fits the printer and parts that are available for use. Throughout the project, the design will be optimised in an iterative fashion, based on the experiences in working with it.

Reading Guide

This report serves as a detailed description of what has been troughout the project, but is also intended as a reference guide for future researches into printing with paste-like materials.

Chapter 2 serves as a deepdive into literature about AM and FDM/FFF to gain a better understanding in the environmental impact it makes and the necessity of this research. Based on this data, later on in the research, an estimation can be made of the reduction in energy consumption that could be made by printing with the material mix.

The third chapter describes the design process of developing the printer modification and the impact that some of the most important parts make. As a lot of parts are somewhat interchangeable, it is important to understand what impact the different options make.

Chapters 4, 5 and 6 belong together as they describe the process that is made in developing material mixes. Chapter 4 talks about the function of the main components in material mixes as well as describing the procedure of preparing materials for use in mixes and the procedure of making the actual mixes. Chapter 5 talks about eggshells and their potential to be used as a component in material mixes. Chapter 6, the last of this trilogy, talks about the journey that has been made in testing binders and additives and developing various material mixes.
Chapter 7 talks about the best found test procedure that has been developed by trial-and-error throughout the project as well as describing the most important slicing settings and the impact that they make.

In Chapter 8, the found material mixes will be assessed based on the criteria that have been defined earlier.

Then in Chapter 9, a final conclusion can be taken about the found material mixes and how well the goals of the project have been achieved.

Finally, in chapter 10, a reflection will be made on personal performance and development in this graduation project.

Videos

In addition to text and pictures to describe and visualise procedures and print results, also QR codes, that link to YouTube videos, can be found throughout the thesis. These videos may help to gain a better understanding of what is described in the text.

List of Abbreviations

AM - Additive Manufacturing
CAD - Computer Aided Design
FDM - Fused Deposition Modeling
FFF - Fused Filament Fabrication
GWP - Global Warming Potential
SEC - Specific Energy Consumption
SM - Subtractive Manufacturing
STL - Standard Tessellation Language

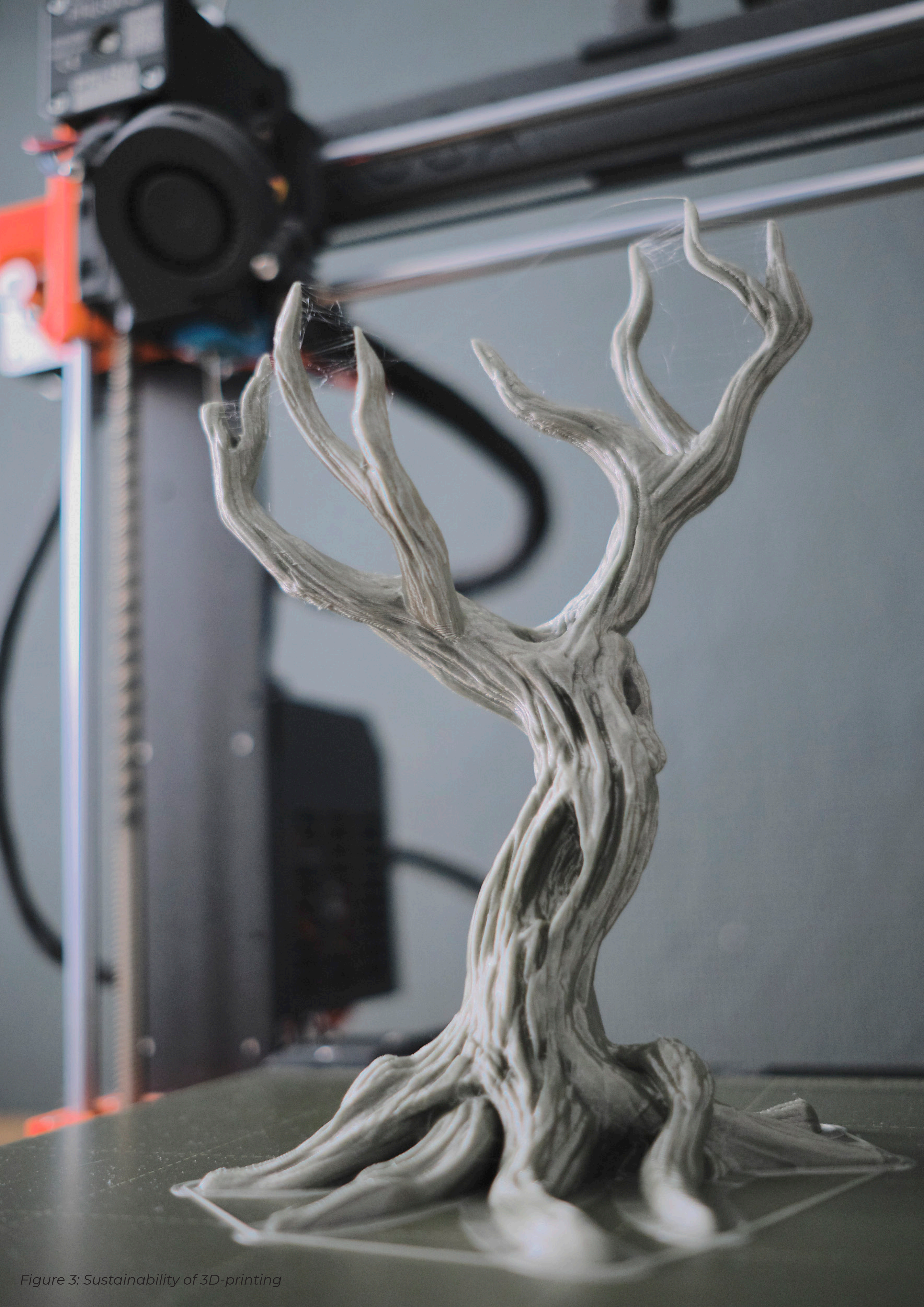


Figure 3: Sustainability of 3D-printing

Ch. 2 | Additive Manufacturing & Sustainability

Additive Manufacturing is often lauded with a child-like wonder for its ability to make the most complex geometries one can think of. The environmental impact of the technology does not seem to get as much attention. To gain an understanding of the sustainability aspects of Additive Manufacturing and see whether any improvements would be desirable, a closer look will be taken at the technology, with an extra focus on Fused Deposition Modeling, one of the more well-known and applied Additive Manufacturing Methodologies

What is Additive Manufacturing?

Additive manufacturing (AM), more commonly known as 3D printing, is a computer-controlled process in which three dimensional objects are created by depositing material, usually in layers. It is not a production technique, but rather a collection of different techniques. The techniques can produce parts and products taking less time and effort, while also being capable of producing complex geometries that could not be made using traditional production techniques (Somireddy, 2018)

The starting point for Additive Manufacturing is a computer aided design (CAD) model that forms the desired object. This model has to be exported into a filetype that can be read by slicer software. There is a plethora of slicer software available and some of them accept more filetypes than others, the most commonly used filetype is STL, which stands for Standard Tessellation Language or STereoLithography. Exporting a CAD model as an STL file, creates a mesh of triangular faces that form a close approximation of that model. This STL file can be opened by the slicer software. In the slicer software several settings can be chosen that decide how the model will be printed. These settings partially rely on personal preferences, such as amount of detail, but also on external factors, such as the used material and the printer model. Once all settings have been selected, the slicer software transforms the model into g-code: an instruction language that can be understood by the 3D printer. The exported g-code is a text file containing all actions that need to be carried out by the printer in order to create the desired model. Once the g-code has been sent to the 3D printer, it will start to print the model. If desired, further processing can be done after the print is finished, such removing support material or sanding the surfaces.

Additive Manufacturing vs traditional production processes

Most manufacturing techniques can be categorized into three distinctive groups: formative manufacturing, subtractive manufacturing and additive manufacturing.

Formative Manufacturing
Formative manufacturing methodologies are most suitable when producing high volumes of the same part. There are high initial costs for producing necessary tooling, such as molds, but the methodologies are suitable for producing high volumes at a low unit price.

Subtractive Manufacturing
Subtractive manufacturing methodologies are most suitable when producing parts with relatively simple geometries at low to medium volumes. These manufacturing methodologies are commonly used when working with functional materials, particularly metals.

Additive Manufacturing
Additive manufacturing methodologies are the youngest of the three groups, first emerging in 1987, are most suitable for low volumes and one-offs. These methodologies are also often capable of producing parts with complex designs that cannot be produced with formative and subtractive manufacturing methodologies.

Although additive manufacturing methodologies are capable of complex designs that cannot be produced with the other manufacturing methodologies, they are currently not suitable as a replacement for the other methodologies in all cases. The production speed of AM is much lower than production speed of the traditional manufacturing methodologies when producing in large volumes and the costs are a lot higher when producing large quantities. Figure 4 gives an indication of the costs per part, relative to the number of parts produced. The costs of parts produced with AM remain fairly constant, regardless of the number of parts produced, whereas costs of parts produced with formative and subtractive methodologies slope down as the quantity of parts produced increases. The break-even points, where producing a part using formative or subtractive methodologies matches the price of a part produced using AM lie at a relatively low number of parts. A majority of the costs for formative and subtractive production methodologies lie in tooling, like molds for injection molding.

Sustainability claims of AM

The sustainability of AM is an ongoing debate. There are several claims why AM techniques could potentially be environmentally friendly production techniques. Commonly used sustainability claims as well as counter-arguments are:

1. AM allows a reduction in resource consumption in production (Annibaldi et al., 2019). However, this claim only applies when comparing AM with subtractive manufacturing at lower production volumes, where material is removed. The embodied energy in the material that is removed generally makes subtractive manufacturing more environmentally detrimental than AM. When comparing to formative manufacturing, which is only suitable for the production of larger quantities, there is no reduction in resource consumption. On top of that, plastic parts are always made through formative methodologies (or sometimes AM) so a comparison with subtractive methodologies makes little sense.
2. AM makes 'just-in-time'-production possible. With conventional production techniques production takes a considerable amount of time so production volume is based on forecasted demand of the product. Any excess production needs to be stored for prolonged periods of time and needs to be disposed of properly. With AM it's possible to produce exactly what is needed when it is needed (Minetola et al., 2018; Cucchiella et al., 2013; Annibaldi et al., 2019).
3. Whereas conventional techniques often need specialized tooling, AM doesn't, making it possible to carry out production more locally, allowing a reduction in transportation in the supply chain (Annibaldi et al., 2019; Cucchiella et al., 2016; Ford and Despeisse, 2016). Although this is factually correct, the impact that transport makes represents only a minor portion of a parts environmental impact throughout its lifetime. Hence the benefit that AM brings in this regard is almost negligible (Faludi et al., 2015; Huijbregts et al.,

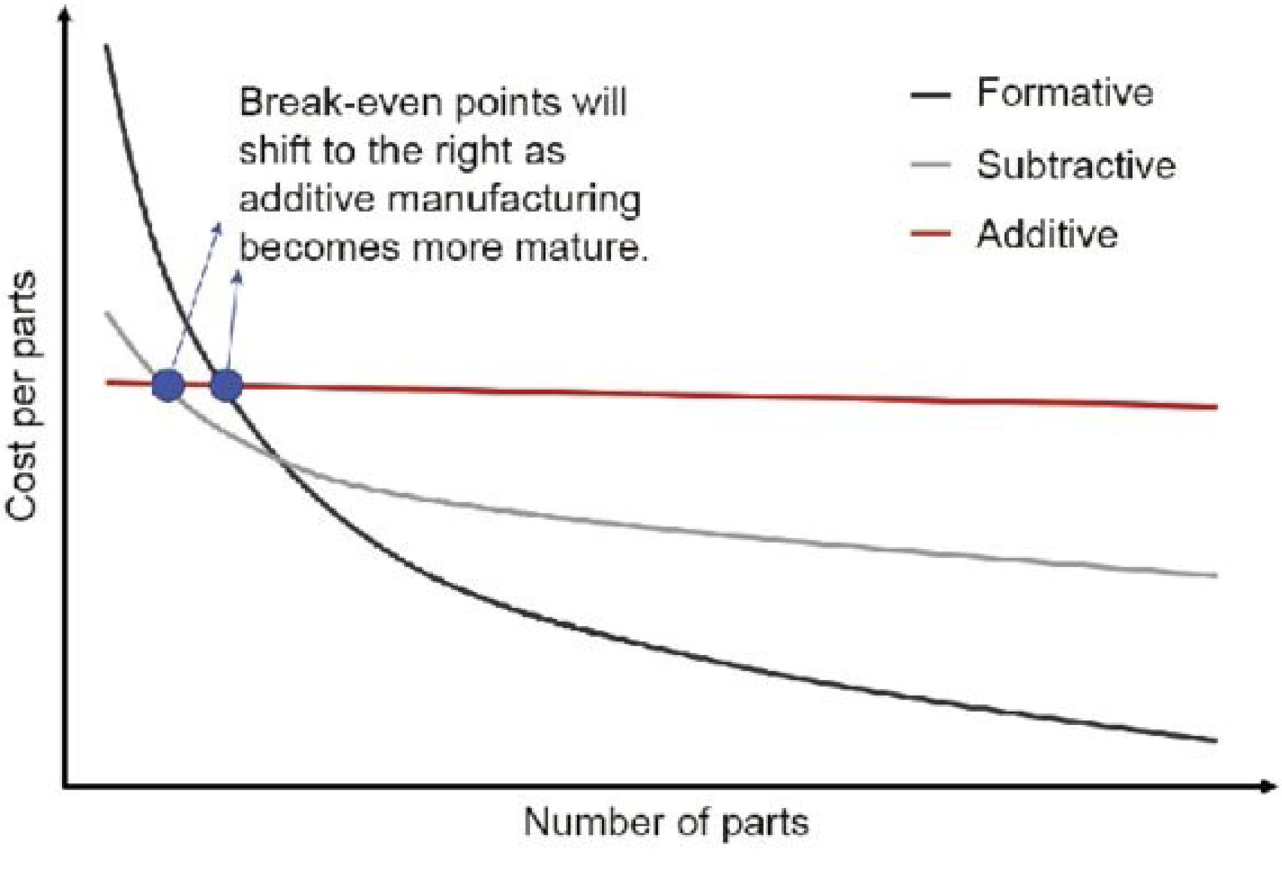


Figure 4: Comparison costs of production methodologies (Ben Wang, 2018)

Figure 5: AM can be used for repairing products (Flipsen and Faludi, n.d.)

2007).

4. Products' lifespan can be extended as AM makes it possible to easily make spare parts. Rather than discarding the product and replacing it with a new one, the product can be repaired, extending its lifespan (Annibaldi et al., 2019). Samenjo et al. (2022) oppose this claim, having found that only 7.5-29% of non-repaired items in repair cafés could potentially benefit from 3D printed spare parts. Other non-repaired items cannot be repaired at all or need parts that cannot be fabricated through 3D-printing.
5. AM enables the creation of complex geometries that cannot be created using conventional production techniques. Assuming this complex geometry is more lightweight than the part(s) that would have been created using the conventional techniques, there are two potential advantages: less resources are consumed in production as less material is needed for the part and a more lightweight part will decrease energy consumption during transport. In aircraft, more lightweight components could decrease fuel consumption considerably (Annibaldi et al., 2019). Again, this is factually true, yet the benefit is only minor as savings in fuel consumption can only be achieved in air- and spacecraft. Application of AM for the production of parts for air- and spacecraft represent only a minor fraction of the total AM use, suggesting that this sustainability claim has little value (Verhoef, 2018). According to American Airlines, reducing the weight of an airplane by 1kg, will lead to an reduction in annual fuel consumption of 114kg (Lyons, 2011).

Environmental Concerns of AM

Focusing on energy consumption of the production methodologies, a different perspective is given. According to Yoon et al., the specific energy consumption (SEC) of AM is roughly 100 times higher than that of formative methodologies, with the SEC of subtractive methodologies sitting somewhere in between. Energy consumption of FDM is not easily quantifiable as it relies on various factors. Earlier research into energy demand in FDM processes by Luo et al., Mognol et al., Baumers et al., Balogun et al. and Yoon et al. resulted in SEC values ranging from 83.1 and 1247 MJ/kg (Kellens et al., 2017). The wide range of results can be attributed to differences in machine tool design (printer model), selected print settings (e.g. layer thickness, print speed), chosen print material (base material and additives), part design and other variables (Kellens et al., 2017).

Fused Deposition Modeling

This report focuses on one specific AM methodology, called Fused Filament Fabrication (FFF). This methodology is also often referred to as Fused Deposition Modeling (FDM). Both represent the same methodology, but the latter name and acronym were trademarked by Stratasys, who invented and patented the methodology. From now on the methodology will be referred to as FDM, as seems standard practice in literature, although either name would suffice.

In FDM a solid thermoplastic, referred to as 'filament', is pushed through a heating element (hotend) to be brought into a semi-liquid state and then continues to move through a nozzle which deposits the material on a build platform following a predetermined path. On the build platform, the material cools down until it solidifies. Layer by layer a three-dimensional part is formed (Redwood, 2020; Annibaldi, 2019).

A distinction can be made between two types of FDM printers: ones with a heated chamber and ones without a heated chamber. The heated chamber forms a stable environment which should lead to more successful prints (Yoon, 2014). Most currently available FDM machines do not have a heated chamber as, up until February 27, 2021, a Stratasys patent (US6722872B1) prevented anyone from selling FDM machines with heated chambers commercially (Sertoglu, 2021). Since the patent has expired, the market has opened for anyone that wants to produce and sell FDM printers with heated chambers.

Figure 6 provides an overview of the thermoplastics that are used in FDM. PLA, PETG and ABS are the most commonly used filaments as they are considered easy to print with, while offering decent engineering properties and being relatively affordable. Thermoplastics higher up the pyramid offer better engineering properties, but are more complex to print with, require higher printing temperatures and are set at a more premium price (Redwood, 2020).

Energy consumption of FDM further defined

To further reduce energy consumption of FDM, it is necessary to have a deeper understanding of the energy consuming parts and activities in FDM. Annibaldi et al. highlighted In their research, Nguyen et al. (2021) composed a model to estimate energy consumption of FDM. They split the printer's components up into three groups: the motors, the heaters and auxiliary components.

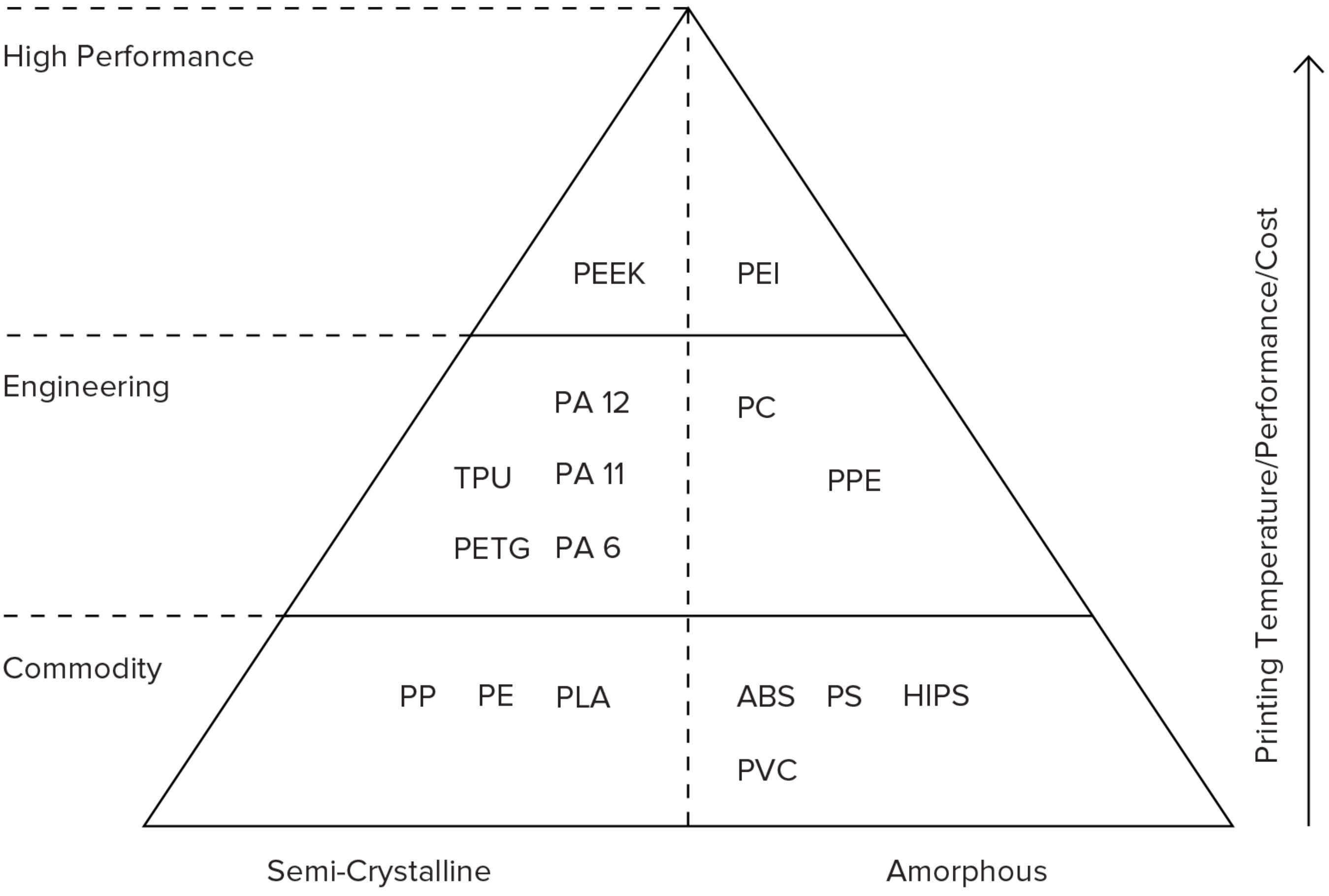


Figure 6: Thermoplastics pyramid (Redwood, 2020)

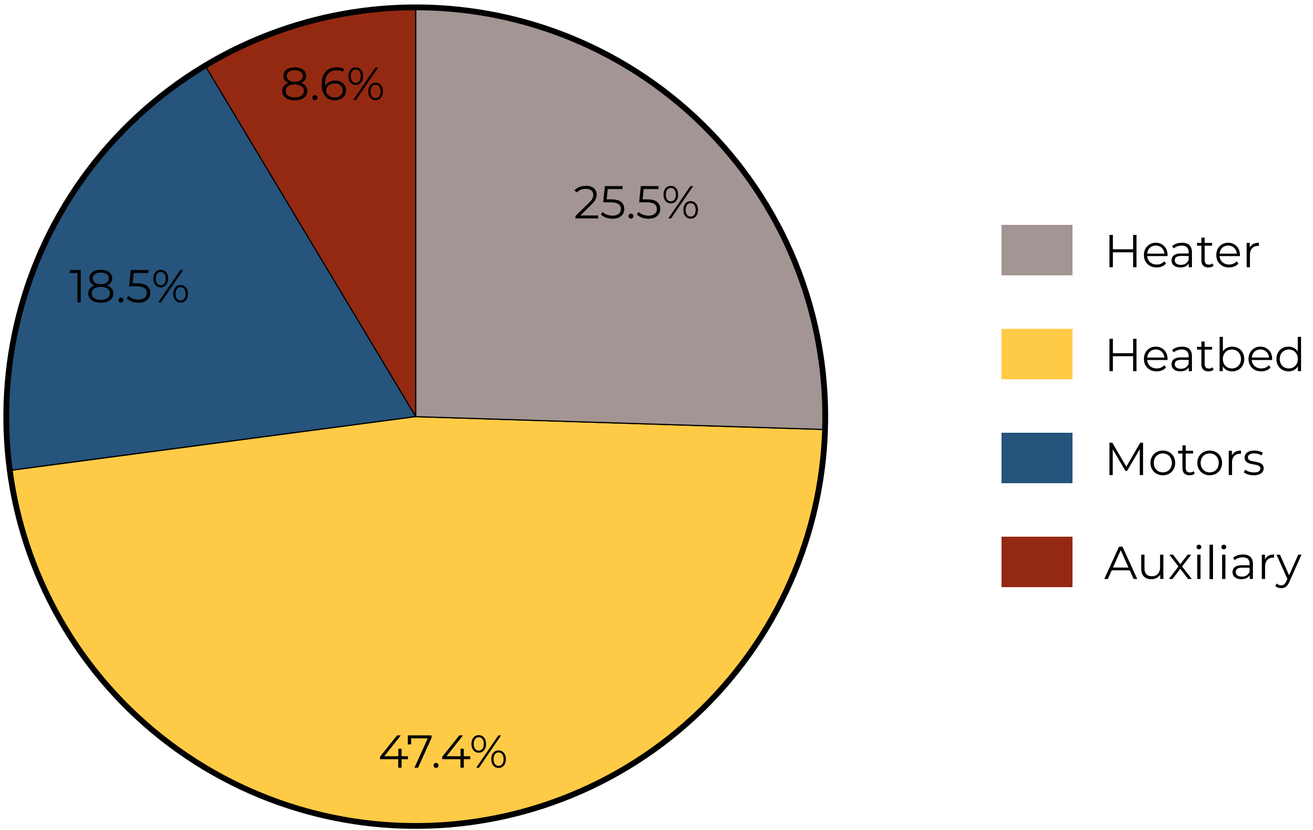


Figure 7: Energy Consumption FDM printer (Nguyen, 2021)

Motors

These are the components responsible for the movement: two for horizontal movement (X and Y), one for vertical movement (Z) and the extrusion motor that supplies material to the printhead.

Heaters

The heaters are the set of components that are responsible for the heating and melting functionality. One heater is located in the printhead, near the nozzle and is responsible for melting the extruded material. The other heater is part of the print bed and its role is to avoid sudden shrinking.

Auxiliary Components

The fans, controller and any other energy consuming components fall in this group. These components have a relatively low power consumption when compared to the motors and heaters.

They found that the heating components are responsible for 72,9% of the total energy consumption of FDM, while the motors and auxiliary components are responsible for 18.5% and 8.6% respectively. See figure 7.

Yoon et al., using a different approach, found that the warm-up process, in which the printer's chamber and nozzle were being heated up to the required print temperature, consumed roughly 60% of the total energy consumption when producing a part with FDM. Energy consumption to maintain the temperature throughout the printing process was measured not separately, but instead was part of the 'Build state', which accounted for 38% of the total energy consumption. It has to be noted that Yoon et al. used a FDM machine (Stratasys 768 SST, Stratasys Ltd, USA) that has a heated chamber in which the printing process takes place. It is pointed out that creating this stable environment increases the SEC of the FDM process. The absence of a heated chamber will likely mean a lower energy consumption in the 'warm-up state'. However, it is also possible that FDM machines without a heated chamber consume more energy to maintain temperature throughout the printing process as the printer bed and hot-end are exposed to the surroundings, which will likely be at room temperature. Unfortunately, no data is available to support this theory.

Nonetheless, regardless whether a FDM machine has a heated chamber or not, heating does account for a major part of the energy consumption of FDM printing. Optimization of the heating functionality of FDM would lead to a considerable reduction of the SEC of FDM, while completely removing the need to heat up printer and material, and with that the components responsible for heating, would lead to an even greater reduction in SEC. However, printing with the currently available filaments at lower temperature is not possible. The filaments need to be brought into a semi-liquid state to be printed with. Table 1 shows the recommended print and heat bed temperature of most available filaments. As can be seen, most materials require print temperatures surpassing 200°C and heat bed temperatures that are considerably higher than room temperature.

Energy-saving strategies for FDM

Various suggestions have been made for energy-saving strategies for FDM:

1. Mognol et al. suggest minimizing the support volume of FDM as an energy-saving strategy, saving up to 61%. The amount of energy that can be saved using this strategy mostly depends on the model's shape and orientation.
2. In experimental results, Nguyen et al. were able to reduce power consumption by 23% by installing the printing process in high ambient temperatures, reducing power dissipation.
3. Ajay et al. (2017) propose a dynamic power gating method that turns off the motor in each axis, when there is no movement in that axis. Nguyen et al. (2021) opposes that, arguing that applying a steady direct current (DC) is needed to overcome residual torque. Dynamic power gating leaves the axis system vulnerable to hold axis alignment in case of vibrations in the system and inertia of the moving parts.

These energy-saving strategies propose strategies to save energy in FDM, but none suggest the use of different materials that have a lower melting point. Although the different researches into energy consumption of FDM vary in their results, they always use one of the commonly used filaments for their tests. Variation in test results can be attributed to slight differences in the material and the additives, among other things. The commonly used filaments are plastics that are easy to print with, are affordable, lightweight and have solid engineering properties, making them suitable for most use-cases. There are currently no materials available that are suitable for FDM and can compete with these properties. The high energy consumption for heating does suggest that it would be desirable to find a material (mix) that is suitable for FDM printing and meets the requirements in affordability and engineering properties for users of the technology, while being able to be printed and solidify at roomtemperature.

FDM Filaments

As mentioned earlier, the more commonly used filaments are PLA, PETG and ABS, which offer a good balance of print-ability, affordability and engineering properties. In the previous section it was established that in the FDM printing process a considerable amount of energy is used to heat these filaments up to their melting point and that it would be desirable to have material mixes available that are suitable for FDM printing, while being able to compete with the commonly used (plastic) filaments. Energy consumption during the printing process is not the only sustainability concern of FDM. The production of the filaments is also a factor that should be considered.

PLA

Polylactic Acid, more commonly known as PLA, is a biodegradable and bio-based aliphatic polyester that finds its origin in renewable sources like corn, sugar, potato, cassava and sugar cane (Castro-Aguirre, 2016; Fortune Business Insights, 2021).

Although the material is still under development and new sources for its production are being explored, the material has been gaining popularity as an alternative for petrochemical-based plastics. This popularity has been driven by two main factors:

4. New legislation forces manufacturers to

Filament Type	Print Temp.	Bed Temp.	Specific Heat Capacity
PLA	*190-220 °C*	*50-70 °C*	*1800 J/kg* K [1]*
ABS	*230-250 °C*	*80-120 °C*	*1390-1410 J/kg*K [2]*
PETG	*230-255 °C*	*50-70 °C*	*1470-1530 J/kg*K [2]*
TPU	*240-260 °C*	*40-60 °C*	*1550-1620 J/kg*K [2]*

Table 1: Thermal Properties commonly used filaments Sources: [1] Xometry, 2021; [2] CES Edupack software;

improve the sustainability of their products and packaging in order to comply with the rules (Castro-Aguirre, 2016).
5. Due to increasing global awareness of sustainability, many customers start preferring more sustainable product choices. Manufacturers have to adapt their products in order attract these customers (Castro-Aguirre, 2016).

However, although PLA is famed for its organic orgin and recyclability, most PLA products end up in landfill (Ghomi, 2021). The biopolymer is technically recyclable, but there is a lack of infrastructure to collect and sort PLA products and packaging (Ren, 2011). In practice, biodegradation and composting are only realized in case the PLA is disposed in an appropriate waste management system. For other composting facilities the challenge of distinguishing PLA from conventional plastics as well as the challange control are arguments not to compost PLA products.

PLA filaments

Most PLA filaments consist of virgin material as recycling of the materials often has a detrimental effect on its mechanical properties. Most FDM filament manufacturers opt for virgin material in order to maintain optimal mechanical properties (Prusa, personal communication). Although rarer, filaments made from recycled PLA are commercially available, most of them only partially being made from recycled material (O'Connel, 2020).

PET(G)

Polyethylene Terephthalate, or PET, is a commonly used plastic that is used for products like soda bottles and report covers. It can be modified by adding glycol, creating PETG (Simplify3D, 2022). The addition of glycol makes the plastic less brittle, more pliable and better resistant to shock and high temperatures than its PET counterpart (ACME Plastics, 2022). Both PET and PETG are made from crude oil and natural gas, meaning their production relies on non-renewable resources. Both PET and PETG are fully recyclable and, in constrast to PLA, there is enough infrastructure to do the recycling (ACME Plastics, 2022). However, research shows that only 11% of PET in Europe was recycled in 2018 (Eugal et al., 2020).

PETG Filaments

However, much like is the case for PLA filament, most PETG filament is made from virgin material as recycled PETG has worse mechanical properties than virgin PETG (Kovacova et al., 2020).

Reference Materials

As mentioned in the introduction, filaments from recycled PLA and PETG, made by Reflow, the client in this project, will be used as reference materials.

Their rPLA filament is 98-100% made from recycled PLA, the exact percentage depending on the colour of the filament. Natural rPLA is 100% recycled, whereas rPLA with a colour are 98% recycled, the remaining 2% representing the colouring agents. The filaments have been made from recycled food packaging, derived from local industry (Reflow, 2022a).

Their rPETG filament is 100% made from serving trays that have formerly been used in hospitals (Reflow, 2022b).

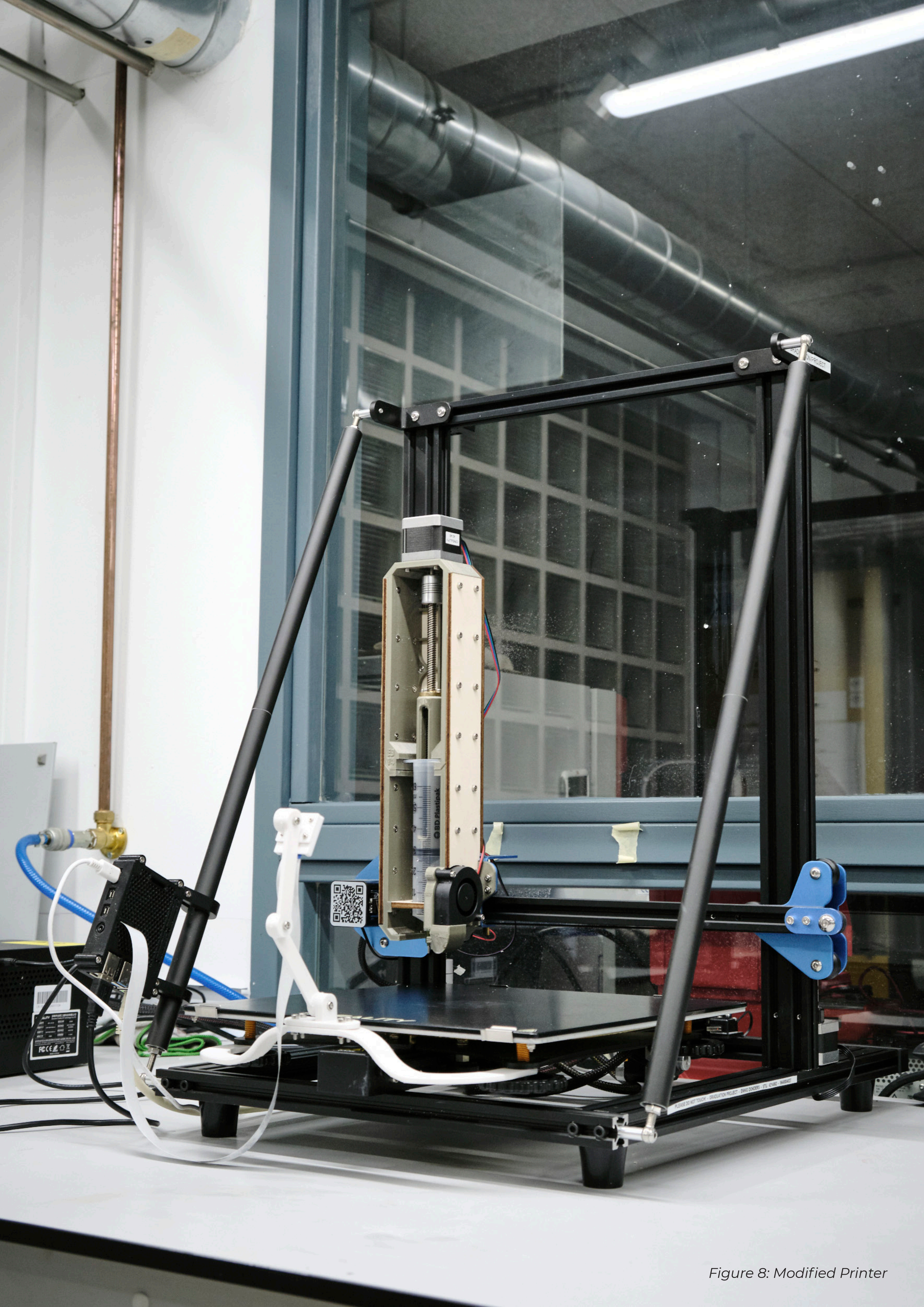


Figure 8: Modified Printer

Ch. 3 | Printer Modification

In order to be able to print with various paste-like material mixes to test their suitability for FDM printing, it’s of course necessary to have a printer that is able to somehow extrude these paste-like materials. In this chapter the process of selecting a printer and modifying it for the project will be dived into.

Printing with paste has been in development for years and there are several paste printers available. The most common use for this printers is to paste with clay, with which models such as vases and sculptures are made. In addition to full printers, there are also modification kits available that can be installed on conventional in order to enable them to print with pastes. An examples of such kits are the ones sold by Stoneflower 3D, who sell both printheads and full modification kits. A distinction can be made in operating principle between the various clay printers and modification kits that are available: some of the printers use motors for extrusion, whereras others extrude using airpressure. For the latter group, an aircompressor would be necessary to provide the airpressure needed for extrusion.

For this project, neither clay printer nor modification kit was available so a conventional FDM printer had to be adjusted in order to enable it to print with paste-like materials. The process of modifying the printer has been a substantial part of the project and several iterations and adjustment have been made throughout the project in order to improve print quality and easy of use of the printer. For the modification it was chosen to have have material extruded by a stepper motor rather than airpressure. This choice was made as motor-based extrusion would be possible with a simpler design, pricing of the modification would be lower, and environmental impact of the modification would likely be lower. On top of that, due to the COVID-19 measurements that were in place at the TU Delft ate the time that the project was started, access to the faculty was limited, especially to specialized equipment such as air compressors, ruling out the option to modify the printer to work with air pressure-based extrusion.

The steps and challenges of designing and developing modifications will be discussed in this chapter. A distinction will be made between modifications to the hardware and software of the printer as both are required to successfully be able to print with paste-like materials. In addition to the printer, a Raspberry Pi with OctoPrint was used for easier control over the printer and the printing process. The process of installing it and the benefits it has brought to the project will also be discussed.

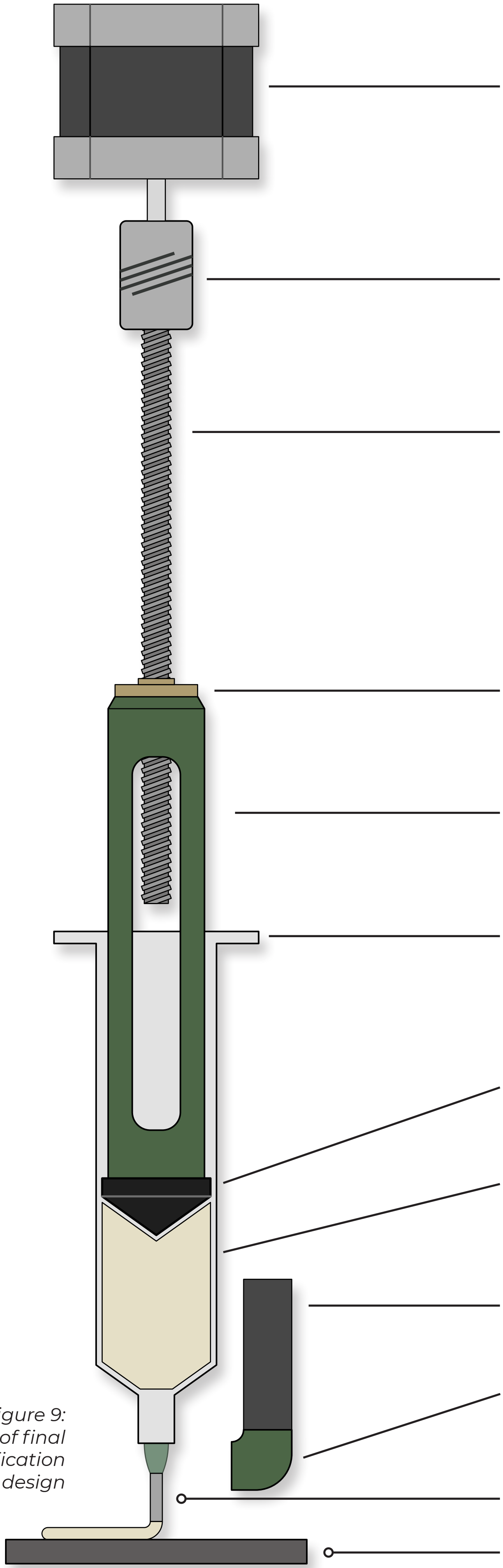


Figure 9: Overview of final modification design

Stepper Motor
~purchased item~
Controlled by printer. Drives extrusion system

Clutch
~purchased item~
Connects motor to lead screw

Lead Screw
~purchased item~
Controlled by motor and supplies motion to other parts

Brass Nut
~purchased item~
Attached to plunger. Drives plunger down due to rotation of lead screw

Plunger
~3D printed part~
Causes extrusion by pressing down on material mix in syringe

Syringe
~purchased item~
Holds material mix

Plunger Cap
~purchased item~
Creates airtight seal between syringe and plunger to prevent material leakage

Material Mix
~developed~
Material mix that is developed in the project

Radial Fan
~purchased item~
Supplies extruded material with cooling to improve drying/solidification

Radial Fan Bracket
~3d printed item~
Brings airflow from radial fan directly to extruded material

Blunt Needle
~purchased item~
Functions as nozzle. Connected to syringe

Printbed
~purchased item~
Flat surface onto which the 3D model is printed

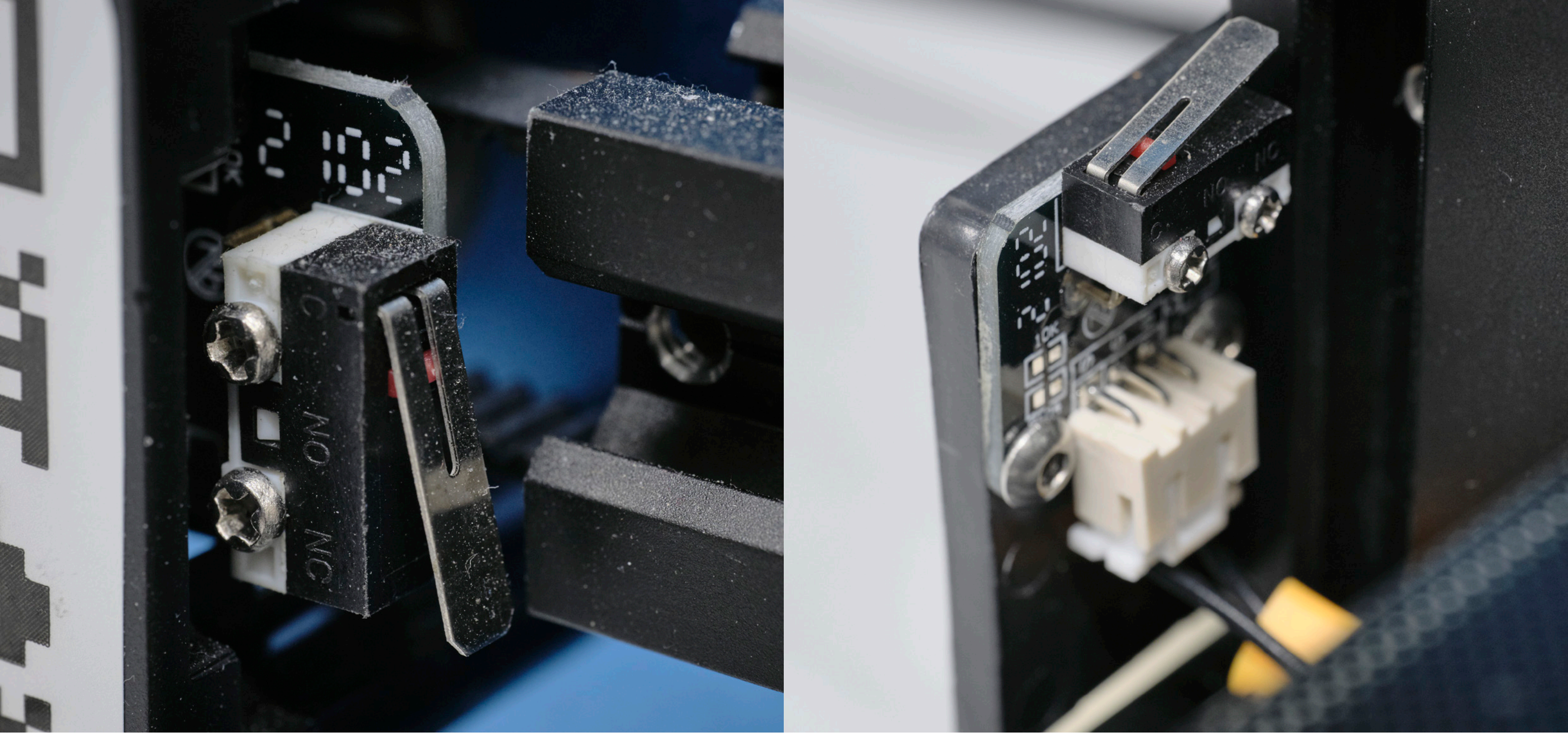


Figure 10: End-stops on Y-axis (left) and Z-axis (right)

Hardware

The printer that was modified during the project was a Creality CR-10 V3. Various iterations have been made of the printer modification, which were all based on a design of YouTuber Constantijn (2019, https://www.youtube.com/watch?v=Q3A4NqTPOYY&t=853s). Throughout the project several iterations of the printer modification were made, which all largely worked in a similar fashion. In this chapter the final modification design will be discussed. Figure 9 shows a simplified version of the printhead with the most important parts.

General Working Principle

On top is a Creality 42-40 stepper motor, which is controlled by the printer itself. The motor drives a leadscrew (with an 8mm lead), being connected to it with the help of a clutch. The plunger is a custom designed, 3D-printed part, that fits inside the syringe. A carriage nut is bolted on top of the plunger, allowing movement of the plunger along the leadscrew. In order to prevent the plunger from rotating around its z-axis, rather than moving up and down along the z-axis, a small rod is placed at the top back, which is placed into vertical rails inside the frame of the printhead. The placement of this rod in the rails prevents the plunger from rotating along with the leadscrew, but instead is forced to move up and down along the leadscrew, depending on the rotation of the leadscrew. The syringe is placed stationary in the printhead and the material mix that is put inside is extruded by moving the plunger down. A fan is placed next to the nozzle, helping to speed up the drying/solidification process of the material mixes used for printing.

In the design, nozzle location was made identical to the design of the original printhead that was supplied with the printer. This allowed the use of the end-stops (figure 10) that are placed on the different axes. End-stops are used for homing the three axes, making them essential for easy calibration of the printer and consistent print performance.

Syringe

Syringes are available in various sizes. What size is best, completely depends on the intended use of the printer. Logically, a larger syringe holds more material and thus is capable of printing larger models without needing to be refilled. In tests it was found that refilling the syringe is a complicated process that often leads to failed prints. The problem being that getting consistent extrusion is challenging and when a syringe is just filled, it will require some tuning to get the material flowing properly. The downside of larger syringes is that it will require a larger printhead, which is usually more unstable and prone to vibrations that could cause defects in prints. On top of that, larger syringes will require more force of the extrusion motor to extrude material and more force of the motors on the axes to which the printhead is attached due to the added weight of the larger syringe, larger amount of material inside the syringe and larger printhead. In this case a BD Plastipak 60mL Luer-Lock syringe was used.

Figure 11: Needle size chart

Nozzle/Needle

Directly related to the syringe, is the use of nozzles. Syringes themselves often have fairly large nozzles and need to be used in conjunction with needles. Much like with standard FDM printing, the nozzle (needle) size is directly related to the print resolution that can be achieved. A larger size nozzle means that the line width and suitable layer thickness are larger as well, resulting in less precision and less detailed prints. Earlier versions of printer modification worked with a syringe with a larger nozzle, which worked fine for printing larger or shapes with less demands on dimensional accuracy. Later versions of the modification used a syringe with a Luer-Lock connection. Luer-lock is a standardized system of small-scale fluid fittings, often used in laboratories and for healthcare. When printing with pastes, short, blunt needles can be used. A shorter needle is recommended as it decreases the chance of paste drying inside it, clogging the needle, whilst also making it easier to clean the inside of the needle after use. Sharp needles should not be used as the angled cut will make it impossible to have smooth extrusion in all directions and could potentially damage the print and print bed. Blunt Luer-Lock needles are available in various sizes and depending on the level of detail needed in the print and the material mix used, the right size can be chosen, similarly to how nozzle sizes are chosen for conventional FDM printing. When choosing larger nozzle sizes, printing can be done faster as linewidth is identical to the nozzle size and with larger linewidth, the same volume can be created with a lower number of lines. Furthermore, with smaller nozzle sizes there is an increased risk of the nozzle clogging up due to paste drying up inside. On the other hand, as mentioned before, smaller nozzle sizes do allow the creation of more detailed prints. For needles, the inside diameter (= nozzle size) is generally indicated in gauges. Table 2 gives an overview of gauge and inner diameter size. During the project needles up to twenty gauge were tested, see figure 11.

Model *(in gauge)*	Outer Diameter *(in mm, ±0.02mm)*	Inside diameter *(in mm, ±0.05mm)*	Total Length *(in mm, ±1mm)*	Needle Length *(in mm, ±0.5mm)*
14	*1.80*	*1.50*	*23.8*	*6.3*
15	*1.80*	*1.37*	*23.8*	*6.3*
16	*1.60*	*1.20*	*23.8*	*6.3*
17	*1.47*	*1.04*	*23.8*	*6.3*
18	*1.25*	*0.84*	*23.8*	*6.3*
19	*1.01*	*0.70*	*23.8*	*6.3*
20	*0.89*	*0.60*	*23.8*	*6.3*
21	*0.80*	*0.51*	*23.8*	*6.3*
22	*0.69*	*0.41*	*23.8*	*6.3*
23	*0.60*	*0.33*	*23.8*	*6.3*
24	*0.55*	*0.30*	*23.8*	*6.3*
25	*0.50*	*0.25*	*23.8*	*6.3*
26	*0.45*	*0.24*	*23.8*	*6.3*
27	*0.40*	*0.20*	*23.8*	*6.3*
30	*0.30*	*0.15*	*23.8*	*6.3*
32	*0.24*	*0.10*	*23.8*	*6.3*
34	*~*	*0.06*	*23.8*	*6.3*

Table2: Needle size chart (Aliexpress, 2022)

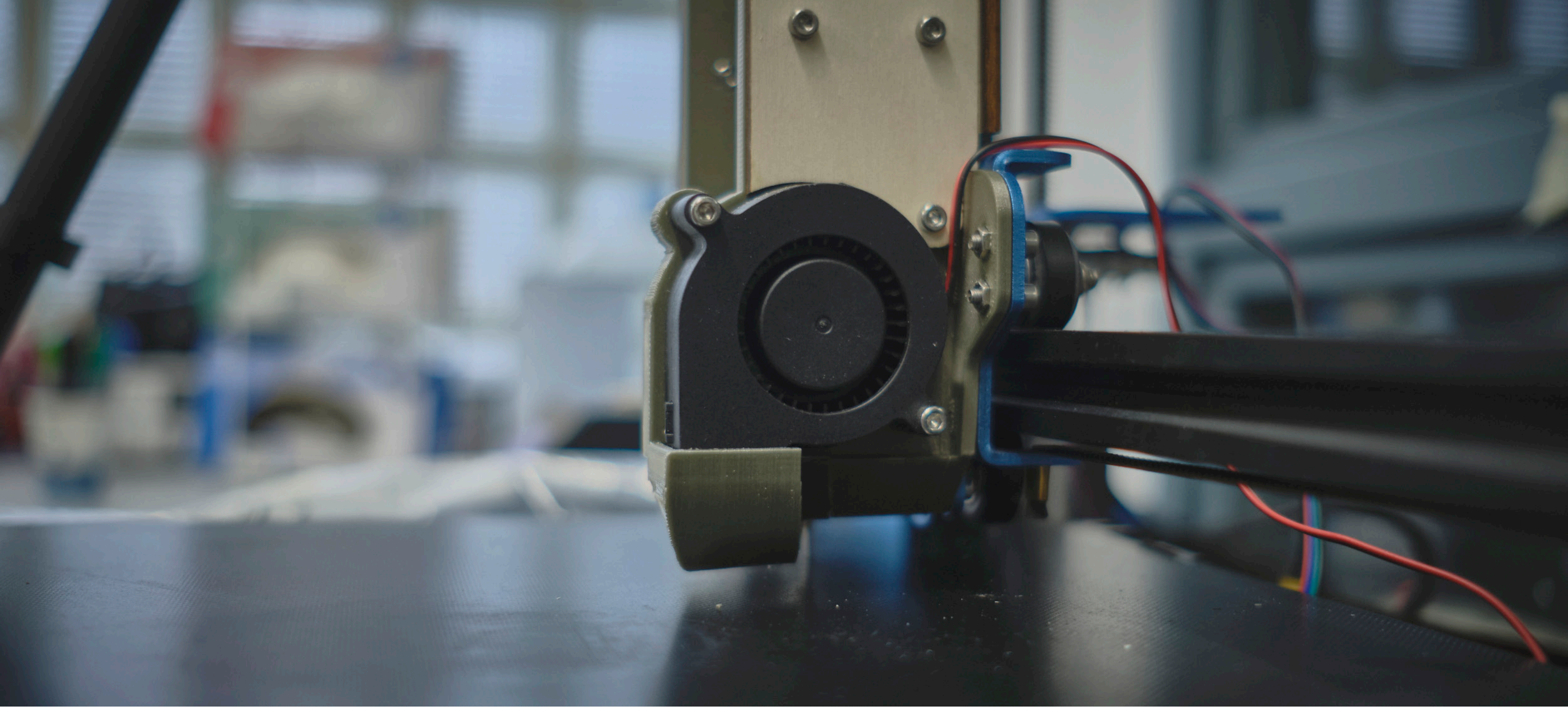


Figure 12: Fan On Side of Printhead

Fans

In earlier stages of the project, it was assumed that the addition of fans would not be beneficial to the printing quality as fans are generally used for cooling the molten plastic filament and hot end of the printer. As no heating was used while printing with the paste-like material mixes and thus no cooling seemed to be needed, there seemed no use for any fans. However, in personal communication, dr. Sauerwein mentioned that fans may help the material mix to solidify/dry faster and by doing that, provide a better print result. This was confirmed by dr. Faludi. Therefore, in later stages of the project, a radial fan was added to the printhead. It was found that a fan can indeed help the material mixes to solidify faster. The fan was attached to the side of the print head, rather than the front, in order to keep easy access to the syringe, while still trying to keep the fan as close to the nozzle as possible. See figure 12. The combination of close proximity of the fan to the nozzle, as well as the addition of a custom, 3D-printed part, leading the airflow from the fan directly to the tip of the nozzle, make sure that the effectiveness and efficiency of using the fan to speed up the solidification of extruded material are maximized.

Print bed

Most FDM printers come with glass or coated metal print beds. Which material print bed is best depends on the filament that is printed with. Some filaments have better adhesion on glass print beds, whilst others have better adhesion with coated metal print beds. For some filaments, such as ABS, it is often recommended to apply glue or hairspray to the print bed, as bed adhesion

Figure 13: Baking paper has been applied to the print bed

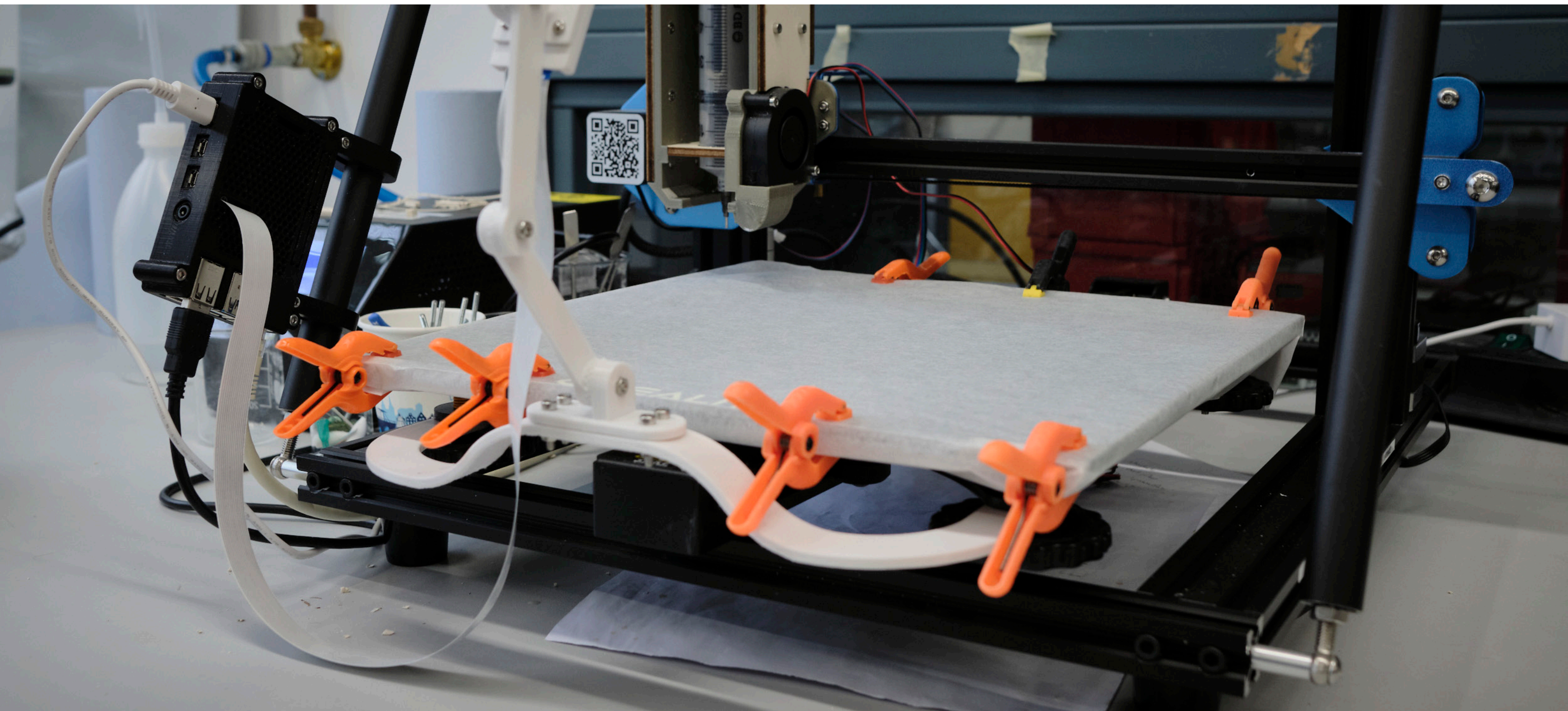


Figure 14: Bottoms of prints. Material mix on baking paper (left), material mix on plastic sheet (middle) rPETG on metal-coated printbed (right)

can be so poor that the print is pulled off the bed during the printing process. Applying the glue or hairspray should increase bed adhesion to a level where the print hopefully sticks to the bed until it is finished. Directly after the print is finished, it should be possible to remove the print from the print bed without much difficulty. In the case of coated metal print beds, the print bed can even be bend slightly to help smooth removal of the print.

When printing with paste-like materials, removal of the print from the print bed is a lot more complex. Whereas prints made with plastic filaments solidify virtually instantaneously, prints made from paste-like material mixes often need more time to fully dry and solidify, ergo directly removing them will likely result in substantial deformation of the print. On the other hand, allowing the prints to dry and solidify before removing them may take a considerable amount of time, during which the printer cannot be used and it may be incredibly difficult to remove the print without damaging or destroying the print or print bed once the print has dried. In prints made with plastic filaments, layer adhesion is generally stronger than bed adhesion, making it possible to remove the print fairly easily without damaging it. For prints made with paste-like materials, bed adhesion and layer adhesion seem more similar in strength, making it difficult to remove the print without deforming or damaging it.

By printing on a removable surface, this issue can be prevented. During most tests, baking paper was attached to the printing bed using clamps (figure 13), allowing the removal of the print from the printing bed so it can dry somewhere else. Once the print has fully dried, detaching it from the baking paper can be done easily due to the slightly greasy coating on the baking paper. From a sustainability standpoint, this is not ideal, as a piece of baking paper has to be used for each print. The environmental impact that this makes could potentially be lowered by carefully handling the paper to prevent creasing and removing all the dried paste so it can be used again for future prints. This was not tested however as the paper seemed drier after being exposed to air for longer periods of time. It can be expected that the greasy coating is (partially) removed when detaching the print and smooth removal of future prints will be more difficult when the paper is reused. Another downside of using baking paper is that wrapping it tightly over the print bed is virtually impossible. Instead, it tends to ripple, resulting in a wavy pattern on the bottom of the print, see figure 14. In personal communication, dr. Faludi suggested the use of transparency sheets, as those are more heavy and less likely to ripple. Former students of his were able to get smooth print bottoms when using these transparency sheets.

As transparency sheets are not as easily available, plastic report covers, made from clear polyester, were used for tests. It was found that they work extremely well, as the prints come out with completely flat bottoms and are easy to remove. The plastic sheets are able to lie completely flat and barely wrinkle, although it's still important to clamp them down. Removal of the prints is really easy and in case that the prints seems to stick to the plastic sheet more, the plastic sheet can be bend slightly to make removal of the print easier. In figure 14 a comparison can be seen between prints made on baking paper, prints made on plastic sheets and rPLA prints made on a smooth PEI sheet.

Software

Most FDM printers run on a modified version of an open-source software. In the case of the Creality CR-10 V3, this is a modified version of Marlin. Commonly made modifications are filling in the dimensions of the printable area, setting up the parts that are installed on the printer (such as calibration tools and direction of the motors) and adding branding visuals to the printer interface. The software helps to run the printer smoothly and makes working with the printer as easy as possible. However, all settings are aligned with how the printer is intended to be used, which is to print with plastic filaments. In the case that the printer hardware is modified and different materials are used to print with, some of the standard settings can actually work against you. The most important changes are discussed below. A link to download the Marlin code can be found in Appendix G.

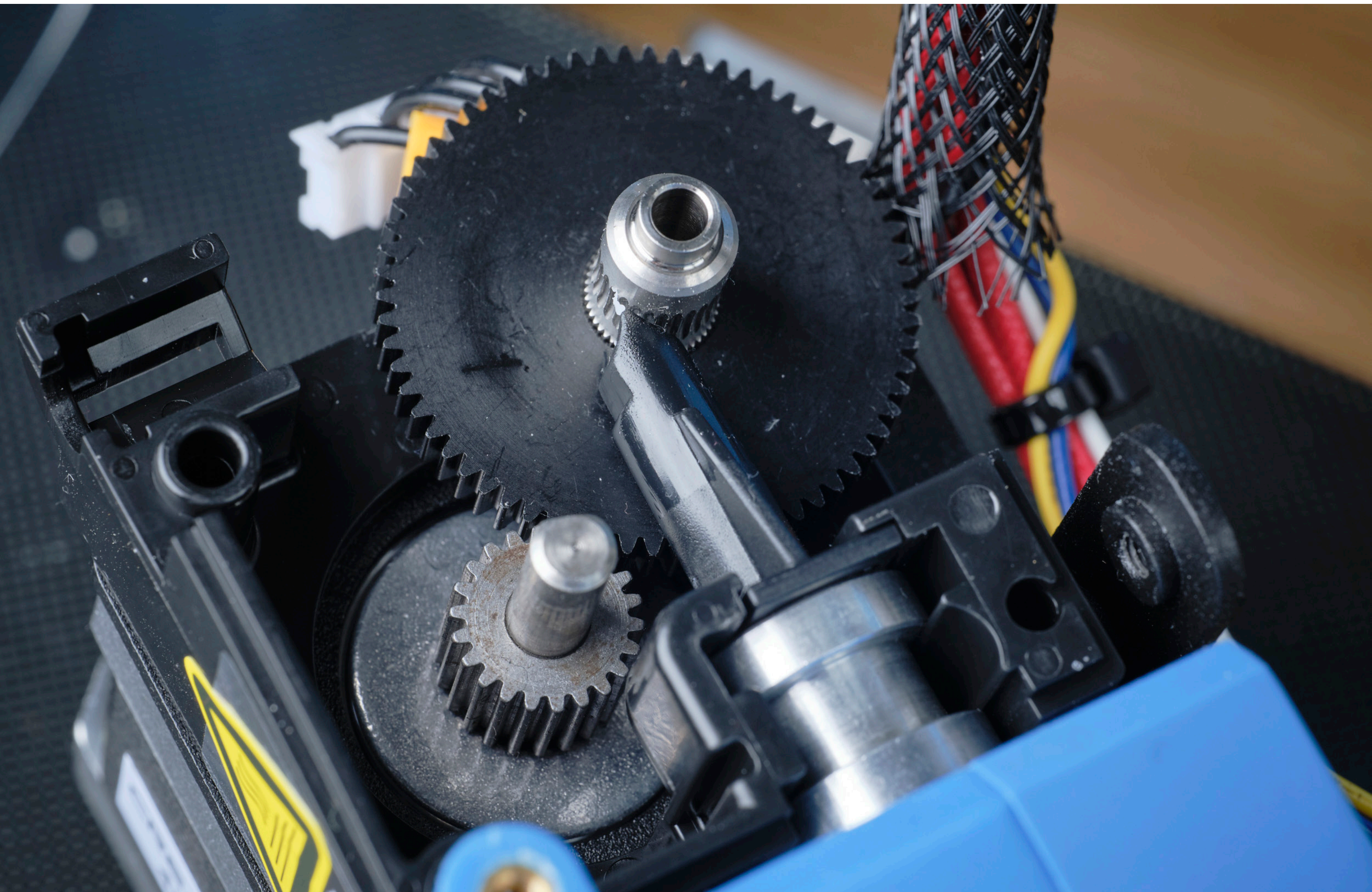
Extrusion Speed

Changing the extrusion speed. The original printhead prints with ⌀ 1.75mm filament. In the modified version of the printer the diameter of the filament is actually the inside diameter of the syringe, which is 26.5mm, considerably larger than the diameter of the plastic filament.

By disassembling the printhead, it is possible to determine how much material is extruded for every full rotation of the extrusion motor. Figure 15 gives an overview of the inside of the printhead, clearly showing the extrusion motor, two gears and a drivegear. From measuring the gears and doing some calculations it is found that for every full rotation of the motor, 20.15mm3 filament is extruded. In the design of the modification, 4400mm3 of paste-like material mix is extruded for every full rotation of the extrusion motor. In order to prevent an extreme amount of over-extrusion, the extrusion speed has to be set to (20.15/4400)*100%=0.46% of the original value. In the case of the Creality CR-10 V3, extrusion speed is normally set to 407, but with the modification installed it has to be set to 1.86.

Theoretically, extrusion speed does not need to be changed inside Marlin as extrusion speed can also be altered using the flow setting in Cura. However, when printing with pastes, the flow rate also needs to be adjusted to compensate for the viscosity of the material mix that is being printed with. When the default value for flow rate is set to 0.46%, further adjustments of the flow rate will be incomprehensible. By adjusting the extrusion speed in Marlin, the default value for flow rate will remain 100% and this is easier to relate with in any further adjustments to compensate for varying viscosity levels.

Figure 15: Inside construction of original printhead



Extrusion Direction

As the design of the original printhead is completely different than the modified version (extrusion motor is oriented differently and gears are used), the extrusion direction could be different too, meaning that extrusion and retracting are switched. By testing the printer, once the hardware of the modification has been installed, it is possible to determine whether the extrusion motor moves into the right direction. In case the direction is wrong, it can be reversed in Marlin.

Cold Extrusion

Disable cold extrusion is a safety feature build into Marlin to prevent extrusion at temperatures lower than melting point of the material that is printed with (Marlin Firmware, 2022). As the commonly used plastics have melting points that are usually above 200 °C, printing with paste-like materials that don't require any heating is prevented by this feature. By enabling cold extrusion, movement of the extrusion motor will be unlocked when printing at lower temperatures, allowing paste-like materials to be printed.

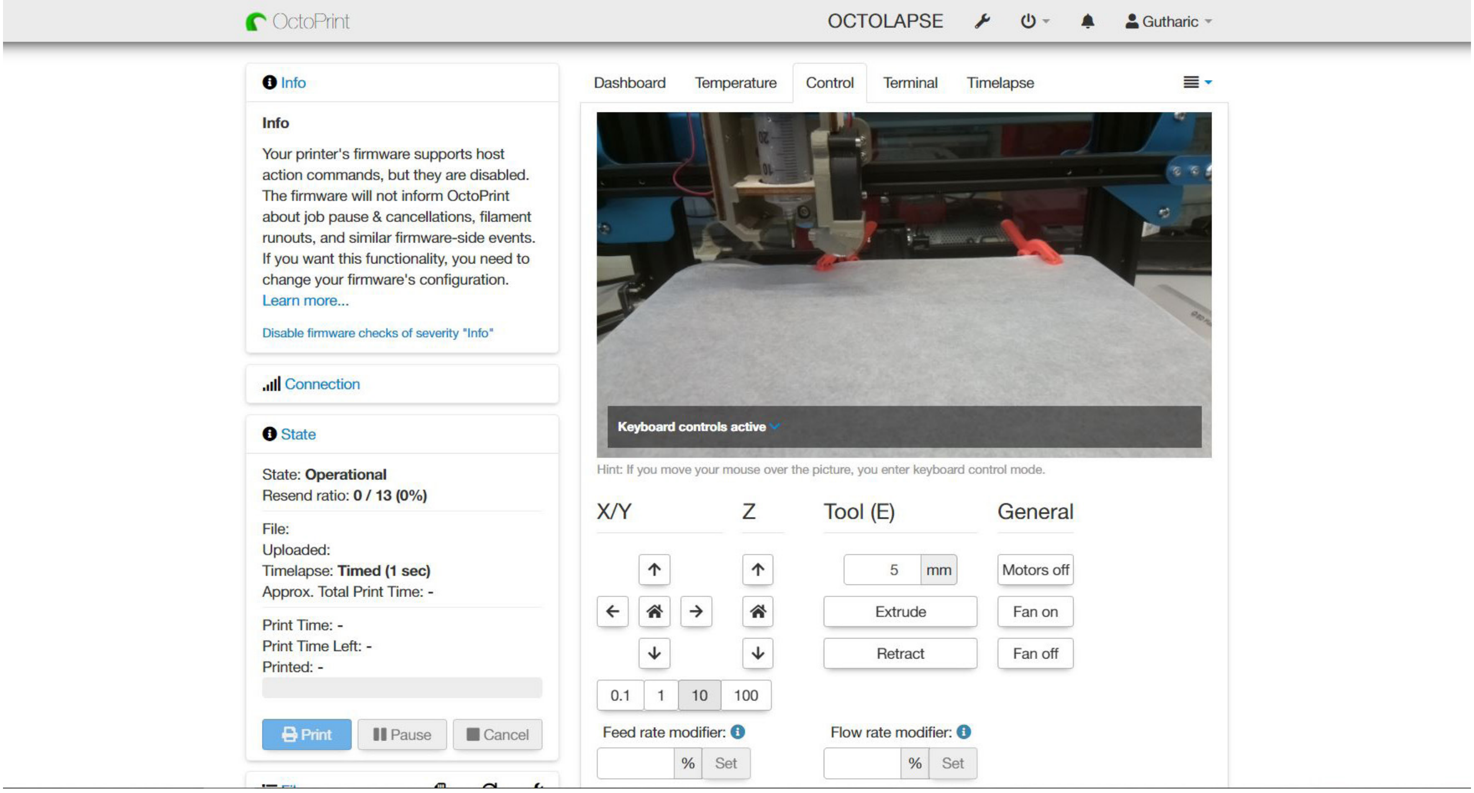
Bed & Hot End Temperature Control

The goal of the project is to find a material that does not need to be heated during the printing process, thus heating elements installed on the printer do not need to be used. Although heating bed and hotend temperatures can be adjusted in Cura (and thus can be set to room temperature), as an extra safety feature, the heating bed and hotend can also be fully disabled inside Marlin to prevent any problems such as printfailure or injuries due to unwanted heating. Although not strictly necessary, this step can be considered.

OctoPi

For easier control over the printer, a Raspberry Pi 4 with OctoPi (figure 17 was used, allowing to control the printer via a webpage rather than via the control unit that is supplied with the printer. This proved to be very valuable as it allowed to easily move around the printhead and make sure extrusion works smoothly before starting a print. The controller on the printer itself also provides this functionality, but control is more cumbersome as movement over each individual axis and the extrusion motor are placed in different submenus, which have to be navigated to and then used one by one, while OctoPi gives the user control over all axes and the extrusion in one overview (figure 16).

Additionally, OctoPi also allowed the recording of videos of the printing process. Throughout the report, QR-codes can be found that link to some of these videos on YouTube. This will hopefully give a better understanding of the process and challenges of printing with paste.



Info

Your printer's firmware supports host action commands, but they are disabled. The firmware will not inform OctoPrint about job pause & cancellations, filament runouts, and similar firmware-side events. If you want this functionality, you need to change your firmware's configuration. Learn more...

Disable firmware checks of severity "Info"

State: **Operational**
Resend ratio: **0 / 13 (0%)**

File:
Uploaded:
Timelapse: **Timed (1 sec)**
Approx. Total Print Time: -

Print Time: -
Print Time Left: -
Printed: -

Hint: If you move your mouse over the picture, you enter keyboard control mode.

Tool (E): 5 mm

Feed rate modifier:

Flow rate modifier:

Figure 16: OctoPi interface with camera view and printer control

Figure 17: Raspberry Pi 4 with OctoPi installed on printerframe

Figure 18: Material mix in the making

Ch. 4 | Material Mix Development

In this chapter the different components of the material mixes are discussed as well as the function they fulfill. Understanding what components are essential or beneficial for developing a suitable material mix will be extremely helpful for reaching the goal of the project. After diving into the functionality of the seperate components, the procedure of preparing the materials and mixing them into a homogeneous paste will de discussed.

Material Mix Components

Material mixes consist of several components that each influence the properties of the resulting mix. These components can be divided into distinctive groups, each with a certain function in the material mix.

Filler

The filler is one of the main components of a material mix often responsible a major wt % of the material mix. Fillers are added in order to enhance certain properties of the material mix, which can be both functional properties, such as mechanical properties, as well as aesthetic properties. Additionally they are often used as an easy way to lower the price of the material mix as they are often materials that are relatively cheap and widely available. In earlier researches materials such as mussel shells (Sauerwein et al., 2020), eggshells (Sauerwein et al, 2020; Otero, 2018) and mica (Faludi et al., 2019) have been successfully used as fillers for FDM printing material mix recipes.

Binder

As the name already suggests, the main function of binders are to bind materials together. Binders supply a matrix for the other materials to latch onto. The most familiar binders are glues, which are used to seperate parts together. Both natural binders, such as sugar (Sauerwein et al., 2020), Xanthan Gum (Otero, 2018) as well as chemical binders, such as sodium silicate (Faludi et al., 2019) have been tested in the past.

It is important to note that not all fillers and binders are compatible.

Additives

Additives are extra components that can enhance certain properties. These may or may not be essential properties. Often used additives are materials that help lowering the viscosity of material mixes, such as water and ethanol.

Functionalization

As a possible extra step, functionalization of material mixes could be tested. Functionalization is a progress during which new functions, features, capabilities or properties are added to a material by changing its surface chemistry (Aerogel, n.d.). A good metaphor would be painting a wall, where aesthetic properties of the wall (colour and texture) are changed. Functionalization would thus be a post-processing step that would enhance certain properties of the print. Examples of functionalization steps that are currently already applied in FDM are painting, smoothing ABS prints using acetone, hydro dipping, epoxy coating and electroplating (Greguric, 2021). An example functionalization of paste-prints is offered by Sauerwein et al. who used alginate to create a water-resistant material through ion cross-linking(Sauerwein et al., 2020). As functionalization is a post-processing step, it's considered an extra step as it will not be a deciding factor whether a material mix is suitable for FDM. It can merely enhance certain properties of prints, potentially making it more suitable for specific applications.

Figure 19: Clean eggshells after rinsing and boiling them

Material Mix Development Process

In this section the steps of creating a material mix will be discussed. Materials that are not already supplied as a fine powder or liquid will first need to be prepared before they can be added to a mix. Think of shells of nuts and fruits for example. The steps of preparing these materials for use are discussed under 'Materials Preparation'. Materials that are already in the form of a fine powder or liquid can be used for creating material mixes without any extra steps.

During the project, most materials were already supplied as a fine powder or liquid, so a number of preparation steps could be eliminated. The pictures that are used in the 'Materials Preparation' section are of eggshells.

Materials Preparation

The first step in making a material mix that may be suitable for FDM printing is preparing the individual components. A number of steps can be necessary in order to prepare a material before adding it to the mix. In case the materials are already supplied in the form of a liquid or fine powder, these steps are not necessary. All of the steps that are discussed below are optional and depend on the material as well as the form it is supplied in.

Cleaning

Cleaning the materials is a very important step as they may contain contaminants that could cause a chemical reaction with other materials, which could potentially change the material mix's properties, or lead the material mix to spoil. An example would be small amounts of leftover food that are still attached to the base material, such as meat sticking to bone, or the pericarp of fruit sticking to the fruit's shell, could lead the base material getting spoiled.

The cleaning is done by rinsing the materials and removing any larger impurities by hand or with tweezers. Availability of industrialized processes for cleaning materials is not always guaranteed, especially if the material is considered waste. In the case of eggshells, currently no industrialized processes to remove egg residue and membranes are available, although they're being researched (Cusack and Fraser, 2002). During the project, when cleaning eggshells, pieces of leftover egg were removed by scratching them off, and then the shells were rinsed until they felt smooth and not sticky. After removing the majority of containments by manually removing them or rinsing them off, the material is boiled for several minutes in order to kill any bacteria. This further prevents the material from spoiling.

Drying

The drying of materials is necessary as it will further prevent the material of spoiling, allows more control over viscosity of the material mix, as there is full control over the amount of fluid that is added, and it's easier to grind dry materials into fine powders. Drying of materials can be done by either air-drying or by putting it in an oven.

As the name suggest, for air-drying, the material is dried by air, meaning it will be placed in a location that is sheltered against rain, where the material sits until it's fully dried. The advantage of air-drying is that no active energy-expenditure is needed, other than the energy needed to build and maintain the sheltered location that is being used. It does however take a considerable amount of time, depending on type of material and the size and thickness of the parts. Logically, a part with a larger relative surface area will dry faster. For wood, it takes about one year per inch of thickness, which goes on to show how long air-drying could take. Drying speed also depends on the conditions of the storage location. Humidity and airflow of the storage location are important factors to consider.

With oven-drying, the drying process is sped up. Whereas air-drying can take days, weeks or even months, oven-drying can be done in up to a few hours. As the boiling point of water is 100 °C, the oven should be set to this temperature in order to maximise drying speed. It is important to check whether the material itself can handle the temperature and does not melt or burn.

During the project, eggshells were put in a Heraeus drying-oven at 100°C for one hour to remove most water contents. See figure 20

Grinding

The finer the material, the easier to mix it well with other materials and the better it attached to the matrix that is supplied by the binder. Materials that were supplied in larger pieces or as a coarse powder, were grinded further down to a smaller size in order to improve their ability to mix well with other materials, improve the homogeneity of the material mixes and thus also improve the (mechanical) properties of the material mixes and the prints that were made with them. Larger particles create weaknesses in the material mix as they cannot attach to the matrix that is created by the binder as well as smaller particles. As a result, the print is more likely to break at places where these larger particles are located when a force is applied to it. This behaviour will be further discussed in Chapter 8.

During the project, materials were grinded with a

Figure 20 Drying eggshells in oven

Figure 21: Materials were grinded into a fine powder

Victorio VKP1024A, see figure 21. Before grinding the materials, they were pulverised as much as possible by hand. Smaller pieces are easily grinded than larger pieces. The mill allows the user to have some control over particle size with a knob that can be set. However, the knob does not quantify the particle size and thus only offers control over it in a more global and relative fashion. In practice it was found that there was quite a lot of variation in the particle size of the resulting powder. A more suitable type of mill would be a ball mill, in which grinding elements travel at different velocities, meaning that there is a lot of variation in collision force, direction and kinetic energy of these grinding elements. The resulting frictional wear, rubbing forces and collision energy act on the particles of the material, grinding them into a fine powder (Neikov et al., 2008). Unfortunately, no ball mill seemed to be available at TU Delft.

Sieving

As mentioned, grinding does not always provide consistent particle sizes, which was also clearly the case for the grinder that was available during the project. In order to obtain a powder with more consistent particle sizes, it needs to be sieved.

Figure 22: Sieving eggshell flour to get more homogeneous particle sizes

Figure : A Proxxon Micromot 40/e with custom mixing bit was used for mixing materials

Sieving was done with a Interlab (ISO3310) sieve with a 0.075mm mesh size. This made it possible to remove most of the larger particles and have more homogeneous powder.

Material Mix Creation

This section describes the procedure of weighing all ingredients and mixing them together into an even, homogeneous paste.

Weighing

Materials were weighed using a Mettler PJ6000 scale at an accuracy of 0.1 grams.

Mixing

Most material mixes were hand mixed using a laboratory spatula. As material mixes were made in small quantities (normally less than 20 mL), most mixers were unsuitable to use. In later stages of the project, spatula-like bits were made that fit on an electronic hand drill, a Proxxon Micromot 40/e, in order to mix materials at high speed (~5000 rpm). Figure 23 shows the custom-made mix setup.

In order to evenly disperse all materials, liquid ingredients were mixed first, before the dry (powdered) ingredients were added. The materials were first carefully mixed by hand until all powder was mixed into the liquids and a seemingly even paste was created. After that the paste was mixed with the electric hand drill at 5000 rpm to make sure the paste was mixed homogeneously.

When mixing it is recommended to to have the mixing bit fully submersed into the material in order to prevent the creation of air bubbles inside the material mix. During tests it was found that while mixing wet/liquid components, there was substantial air bubble forming while mixing with the electric handdrill (see figure 23). However, when the dry ingredients were added to the mix, there was no clear visual evidence of air bubble forming. Also, if the mixed wet/liquid ingredients were left for a few minutes, the air bubbles would disappear. To prevent air bubble forming, more shallow mixing bits have to be used or larger amounts of material mix have to be made. In most tests 10-20mL of material mix was made at a time, so various design for shallow mixing bits were made and tested.

Figure 23: Eggs

Ch. 5 | Eggshells

As stated in previous chapters, the goal of this research is to develop a material mix that is suitable for FDM, could serve as a more sustainable alternative to the commonly used plastic filaments and fits in a circular economy. In order to reach this goal, materials in the mix should be derived from waste streams and be available all across the world in order be able to make the mix locally, limiting the impact of transport. One of the materials that meets these criteria are eggshells. Their potential as a filler for sustainable FDM printing will be discussed in this chapter.

Eggs are a cost-effective and high-quality resource of several nutrients that is suitable for daily human consumption. They are available all across the world and are produced in controlled environments and conditions in most countries. In this chapter eggshells will be further explored to better understand the potential of the material for environmentally sustainable FDM printing, its potential to be part of a circular economy, as well as its availability.

Egg Anatomy & Eggshell Composition

A variety of animals lay eggs, but the ones most commonly known to us are chicken eggs. On average, chicken eggs weigh approximately 60 grams and the eggshell is responsible for around 9.5-11 wt % (Ahmed et al., 2021; Cree and Rutter, 2015; Laca et al. 2017; Nimalaratne and Wu, 2015; Stadelman, 2000). Figure 24 shows an overview of

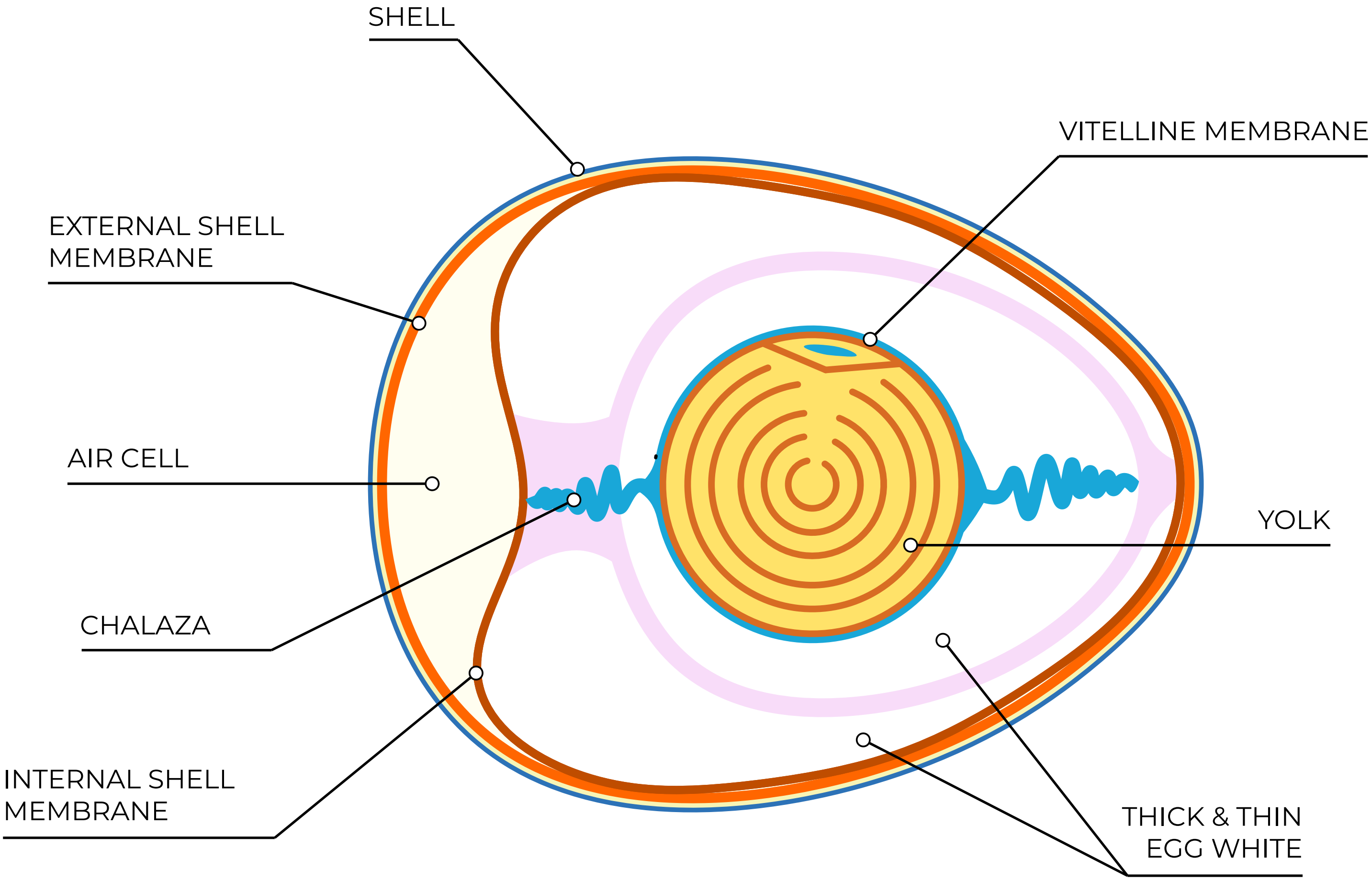


Figure 24: Egg anatomy (Hincke et al., 2022)

the anatomy of an egg as well as the names of its components.

Eggshells consist for 96-97% of a mineral of calcium carbonate ($CaCO_3$), with the remaining 3-4% being a mix of organic matter, including other minerals such as potassium, phosphorus and magnesium (Butcher and Miles, 2018). The mineral in eggshells is a relatively pure version of calcite, the most stable polymorph of calcium carbonate (Cree and Rutter, 2015). Other calcium carbonates often contain a lot of impurities. Limestone for example often contains impurities such as clays, sands and other minerals (Cree and Rutter, 2015).

Calcium carbonate minerals belong to the family of technical ceramics (CES EduPack, 2019) and there are three types: aragonite, calcite and dolomite. With a pH between 8 and 9, they're slightly acidic (National Center for Biotechnology Information, 2022). Furthermore, the minerals are practically insoluble in water (National Center for Biotechnology Information, 2022). The material often combines stiffness, low weight, strength and toughness, but as it's a naturally occurring material, it is not possible to guarantee uniformity of the properties (CES EduPack, 2019).

In assessing mechanical properties of eggshell, often the shape of the egg is also considered. Due to the dome-like curvature of eggs, they are capable of withstanding large compressive forces applied on their major axis (Hahn et al., 2017).

Global Egg Production

Having eggshell be the main component of a more environmentally sustainable material mix for FDM printing is only possible if there is enough supply of the material to meet the (potential) demand of FDM material use. Eggs are used all across the world and are used for consumption in most countries and cultures. The total global egg production in 2020 was roughly 1.4 trillion eggs ($1.4445 * 10^{12}$ eggs). The top 3 leading egg production countries in 2020 were China, India and Indonesia, which were responsible for 41.29%, 7.92% and 7.76% of the total egg production respectively. Figure 25 shows an overview of the leading egg producing countries in 2020.

The utilization of each egg is based on its quality. Eggs graded into different categories, based on their interior and exterior. Different grading systems are used across the different countries and regions, but other than in naming convention, most grading systems are fairly similar. In Canada, eggs that are suitable for consumption are graded into three categories. Eggs that are typically perfect fall into grade A. Eggs with a rougher surface, a flattened yoke, or watery whites fall

Figure 25: Leading egg producing countries worldwide in 2020 (Statista, 2022)

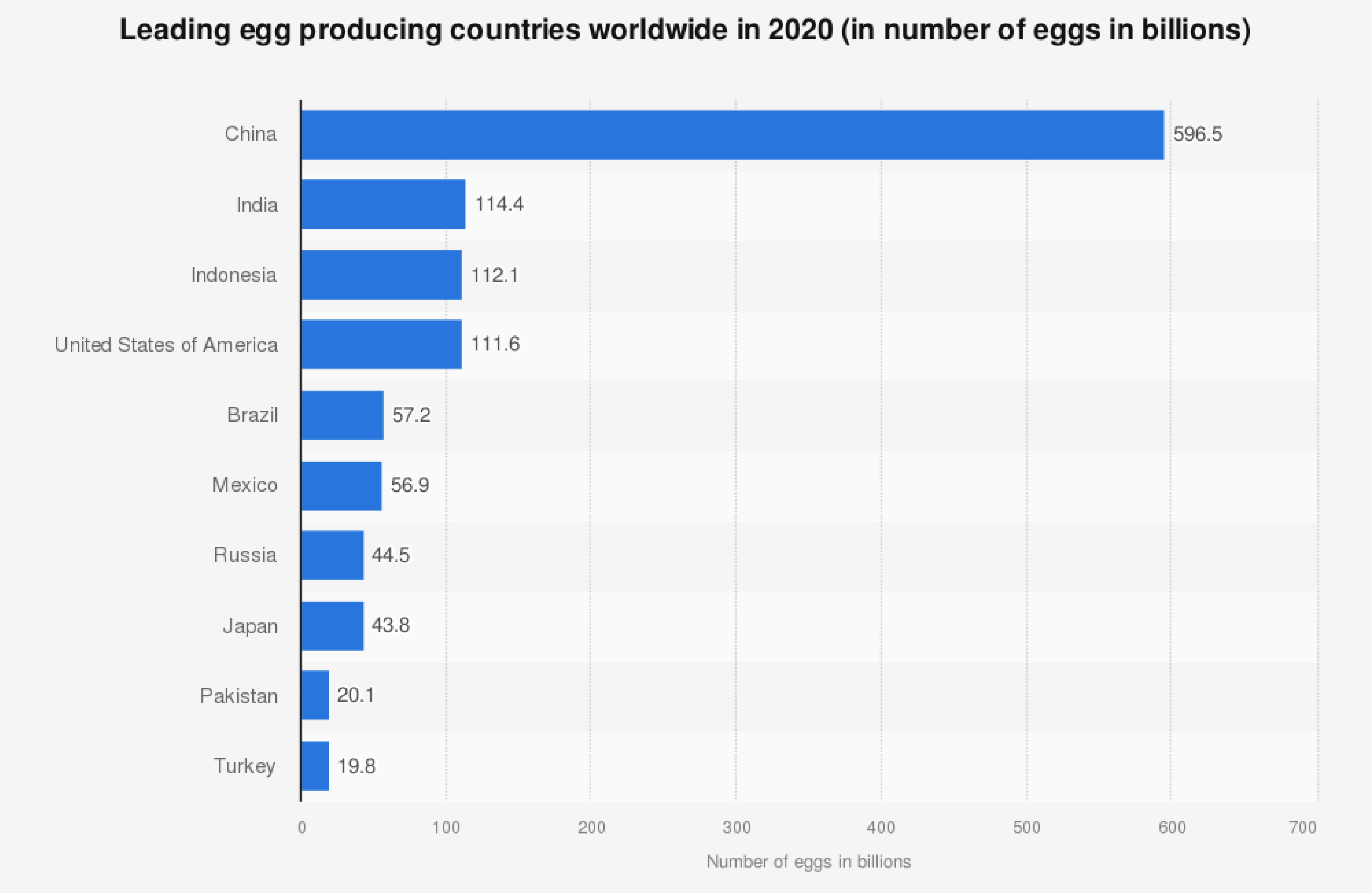


Figure 26: Egg seperation at breaker plant (Aaron Equipment Company, 2022)

into grade B. Grade C contains eggs with loose yolks and cracked, deformed or stained shells. Regardless of what grade they get, all of these eggs are suitable for human consumption. Grade A eggs are sold directly to the consumers for household use, whereas grade B and C eggs are sent to breaking plants. Breaking plants are industrialised facilitities where eggs are mechanically broken and the eggwhite and yolk are seperated from the shell so they can be used for the production of various products, such as mayonnaise, ice cream, baked goods and noodles as well as non-food items.

If the material mix for FDM printing is to be produced at larger scales, only eggshells from eggs that are used for industrialized production of food and non-food items and the ones that go to breaking plants, can be used. In developed countries, about 30% of chicken eggs produced are sold and sent to these breaking plants (Ahmed et al., 2021; Ahmed et al., 2019b; Cree and Rutter, 2015; Kulshreshtha et al., 2020; Tsai et al., 2016). Based on these numbers, it's possible to calculate the potential amount of eggshell that can be saved.

Total Eggs = 1.44... * 10^{12} eggs

Eggs sent to breaker plants = 30% of 1.44.. * 10^{12} = 0.43... * 10^{12} eggs

Weight eggs at breaker plants (in kg) = 0.43... * 10^{12} (eggs) * 0.060 (average weight egg) = 26.0... * 10^{9} kg

Amount of eggshell at breaker plants (in kg) = 10% of 26.0... * 10^{9} = 2.60 * 10^{9} kg

So even though most eggs are sold to consumers for household use, losing its potential to be used in a circular economy, the amount of eggshell that is kept within the industry is still considerable. In the next section current applications of eggshells will be further discussed in order to better estimate the feasibility of using them for FDM printing.

Eggshell Flour Applications

Most eggshells are disposed of in landfills, posing substantial costs to the egg processing plants. In the US, disposal of the eggshells is costing approximately $100,000 annually for each of the egg processing plants (Sonenklar, 1999). Part of the eggshells are used however, for various purposes.

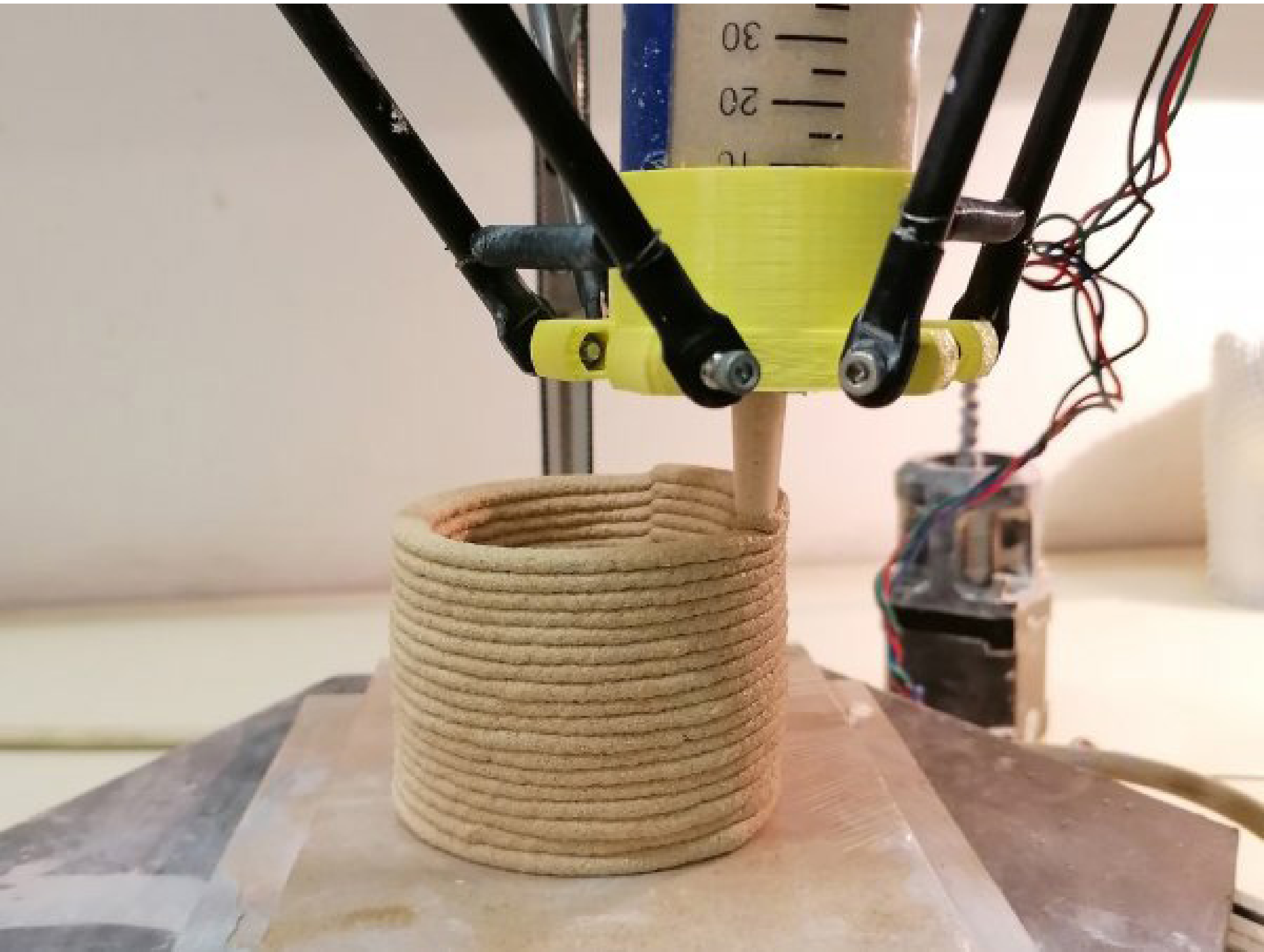
Currently, eggshells form an acceptable source of limestone for crop production, as the calcium carbonate is a crucial mineral for strengthening plants' cell walls and other minerals in eggshells, including potassium, phosphorus and magnesium,

Figure 27: Second print from the left was printed with eggshell flour (Sauerwein, 2020)

also help plants grow (Cree and Rutter, 2015; Finley, 2022). Eggshells can also be used as a source of calcium for chickens, pigs, dairy cattle and pets (Cree and Rutter, 2015). Adoption of eggshells in the diet of laying hens significantly improves egg production (Sim et al., 1983). Nonfood uses of eggshells are addition to cohesionless soils for stabilization analysis (Cree and Rutter, 2015; Okonkwo et al., 2012), ceramic wall tiles (Freire and Holanda, 2006), fillers for inepoxidized natural rubbers (Intharapat, 2013), fillers for polypropylene composite (Toro et al., 2007), cement mortar (Beck et al., 2010) and cement paste (Jayasankar, 2010).

On top of that, in the last few years exploration of uses of the eggshell waste has gotten a lot of attention and the number of patents that describe eggshell-based applications has greatly increased (Adams et al., 2021). Some of the patents describe the use of eggshell for various value-adding purposes, while others describe ways to clean, separate or process the eggshell into powders. However, even though new potential value-added applications for eggshell are being found, the

Figure 28: Ana Otero printing with eggshell flour and xanthan gum (2018)



material is still undervalued (Ahmed et al., 2019a; Ahmed et al., 2021; Cordeiro and Hincke, 2011).

Potential for FDM

The use of eggshells and similar materials has already been tested in the past with various rates of success.

Ana Otero (2018) was able to successfully FDM print with a material mix based on eggshells, water and Xantham and made her recipe available through Materiom.

Sauerwein et al. (2017) were able to successfully print with mussel shells. Like eggshells, mussel shells are composed of a high amount calcium carbonate. Mussel shells can be even more pure as they consist for 95-99% of layers of calcium carbonate, while held together by 1-5% of organic matrix (Barros et al., 2008). Earlier on in their research they also successfully printed using eggshell powder. Figure 27 shows some of the prints that Sauerwein et al. (2020) were able to produce, one of which being made with eggshell powder.

Potential Hurdles

On laboratory level, membranes can be separated from the eggshell, but there are currently no techniques that are suitable for industrialized scales and mass production. Whether removal of the membrane is necessary depends on the application of the eggshell waste. When using it as a supplement for animal diet, the presence of some impurities is no issue, but for some more specific applications it could pose a problem. For the use in FDM material mixes, the impact of the membrane will have to be tested as there is no data available that describes the difference its presence makes.

In case the presence of the membrane is detrimental for the print results, production of the material mix beyond laboratory-scale will depend on development on development of technologies to separate the membrane from the eggshells on industrial scale successfully.

Also, as mentioned in the section ‘Eggshell Flour Applications’, although current applications of eggshell flour are limited and large amounts end up in landfill, there have been a lot of patent applications in the last few years that mention the use of eggshell waste. This trend could potentially limit the possibilities to use the material for FDM in case other uses are financially more rewarding. For example, collagen, one of the materials that can be obtained from eggshells is worth as much as $1,000 per gram (Cree and Rutter, 2015). However, considering the huge amount of eggshell that is theoretically available and the currently limited number of applications, it is unlikely that there will be a shortage of the material any time soon.

Conclusion

Eggshells are a material source that could fit perfectly in a circular economy. Eggs are part of the diet of most cultures and in most countries, so they are available worldwide, enabling local production of a FDM material mix containing eggshell flour all over the globe. The eggshells currently form a large source of waste, as demand does not meet the supply. Although the number of patents mentioning the use of eggshells has increased substantially in the last few years, it is unlikely that there will be a shortage of them any time soon. The added benefit for egg breaker plants is that they could actually make money from the eggshells, instead of them being an expense.

The good mechanical properties of calcium carbonate, the main component in eggshells, could potentially lead to good mechanical properties in the prints that are to be made with it. As eggshells are great soil fertilizer and significantly increase egg production when fed to hens, the material is suitable to circled back into the production cycle, where it helps in the production of new materials. However, whether the material mix can be added to soil or fed to hens directly, will depend on which other materials are added to the material mix.

Figure 29: Print from mixture of eggshell powder and sodium silicate

Ch. 6 | Finding Suitable Binders

Now that eggshells have been chosen as the filler for material mix, the next step is to find binders, and potentially additives, that pair well with it. Through a process of trial-and-error, several binders have been tested on their compatibility with eggshell powder and their suitability for FDM printing in order to find a combination that leads to succesful prints. The process of selecting and testing the different binders will be discussed in this chapter.

Several binders were tested in various ratios in order to see how wel they combine with the eggshell powder and suitability of the resulting mixture for FDM printing. Binders were chosen based on results from other researches as well as how easily they were available.

Initial Testing

Earlier on in the project, when it was not yet decided to use eggshells as a filler, several tests with other fillers have been done, such as pecan shell flour. A recipe was provided by Jeremy Faludi that had been developed by a group of students that he had guided in the past, which was used as a starting point for testing. Their material mix conists of pecan shell powder, calcium lignosulfonate, ethanol, Elmer's Glue and water. It was found to extrude well and result in crisp prints with smooth textures, see figure 30 and 31.

Binder Testing

Once eggshells had been chosen as a filler, the focus shifted to finding a suitable binder. Several binders have been tested, that were selected on their availability, literature and recommendations by experts.

Elmer's Glue

Elmer's Glue is a type of polyvinyl acetate (PVA) that is suitable for the use by children. This glue was provided by dr. Jeremy Faludi and had been used in the material mix by his former students. In tests it seemed to generally mix well with other ingredients, but drying speed was slow. Combinations with eggshell did work decently but due to the low drying speed, it would not provide much support for next layers. This could be solved to some extent by lowering the print speed, giving the material more time to solidify before the next layer was put on top of it, but this would greatly increase printing time.

Woodglue

Woodglue is also PVA and different types have been tested. It was found that the simpler types of woodglue were suitable for use, while water resistant types of woodglue were not. Water was used to decrease viscosity of the material mixes in order to improve flow. Water resistant woodglues would not mix well with other ingredients, especially water and extrusion would not be consistent. As small amounts of glue would be encapsulated by other ingredients of mixtures, drying speed would differ accross the mixtures, resulting in grainy textures accross the print, see figure 32. Therefore, water resistant types of woodglue are not recommended to be used if water is used to decrease viscosity of the mixture. Combinations of just woodglue and a filler were found to be too viscous however, so some sort of liquid to decrease viscosity was needed. As water was found to generally be good for this purpose, testing with water resistant woodglues was soon stopped.

Potatostarch

This starch is made from potatoes and was made in powdered form. The powder was mixed with cold water to make a gel-like mixture with a homogeneous conistency. After that is was mixed with the eggshells until again a homogeneous mix

WATCH ME BEING PRINTED!

Figure 30 & 31: Print with recipe from former students of dr. Jeremy Faludi

WATCH ME BEING PRINTED!

Figure 32 Print with waterproof woodglue

was achieved. Compared to other mixtures, mixes with potato starch seemed to have relatively high adhesive qualities. Extrusion was only possible at slower speeds and the mixture tended to stick to the nozzle too, making printing with it difficult. On top of that, drying speed was extremely low, so building higher models is difficult as the mixture cannot provide enough support for next layers if it has not fully dried. At normal printspeeds, models would not take shape while printing and at low print speeds, the print would take shape, but started collapsing as the print progressed.

Cornstarch

As the name suggests, this type of starch is made from corn. Similarly to potatostarch, cornstarch has to be mixed with water in order to make into a suitable binding agent. Print results were also similar to those with potato starch. Drying speed was too low to provide support for additional layers and prints would collapse during prints or after the print had been finished.

Xanthan Gum

Xanthan gum is a polysaccharide that is used as a thickener or stabilizer in food. Xanthan gum is not found in nature, but is made by fermenting carbohydrates such as glucose or sucrose, using bacteria (Livingston, 2020). It has previously been succesfully combined with eggshells for FDM printing by Ana Otero (2018). During the project is was found to dry too slow and no succesfull prints have been made with it. Material tended to clog around the nozzle and printers were deformed by sagging and the nozzle pushing through the still wet material, see figure 33

Waterglass (sodium silicate)

Sodium silicate, more commonly know as waterglas, is a chemical compound that mixes very well with water. In other research into printing with paste, it had succesfully been used as a binder in combination with powdered mica (Faludi, 2018). It also has a connection with eggs as it was used as a preservative for eggs in the past. When dilated in water in a 1:9 ratio, eggs can be preserved for up to five months (Hall, 1945). In initial tests, mixtures between eggshell and waterglass seem to work decently well, but drying speed was too low to properly print with it. However, during these initial tests, no fan was being used on the printer yet. Addition of the fan increased the drying speed significantly, making is possible to print at reasonable speeds without running into the risk of the print collapsing. As this was the only binder that was found to dry fast enough to be able to provide enough support for additional layers including overhang, it was chosen to be used for further development.

Additive Testing

In addition to testing binders, also the use of additives was researched.

Vinegar

In order to reduce brittleness of the eggshell

Figure 33: Print with recipe from former students of dr. Jeremy Faludi

powder, it was mixed with vinegar. Bone and horn can be made permanently rubbery by soaking them into vinegar (CES Edupack, 2019). As bones, much like eggshells, are mostly made out of calcium carbonate, it was considered possible that vinegar could potentially help make the material mixes with eggshells less brittle. Various tests have been done in which water was (partially) replaced by vinegar. Unfortunately, it was not found to help reduce brittleness of the material mixes. On top of that, some binders, such as xanthan gum and cornstarch, did not dissolve well in vinegar and small particles would float around in the mixture.

According to prof. dr. ir. Kaspar Jansen, vinegar did not help reduce the brittleness of mixtures with eggshell as the calcium carbonate would fully dissolve in the vinegar. Bones and horn also contain cartilage and that what is responsible for bones and horn to become permanently rubbery when soaked in vinegar. (personal communication, April 6, 2022)

As binders would often not dissolve well in vinegar and the brittless of the material mixes was not decreased by the addition of vinegar, its use was stopped at some point.

Glycerol/Glycerine

Glycerol/glycerine is a naturally occuring alcohol. According to a specialist at the OLVG hospital in Amsterdam, who wants to remain anonymous, glycerine is what makes baby bones very rubbery, making them less prone to break during birth (personal communication, December 20, 2022). He recommended trying to use glycerine in order to reduce brittleness of the material mixes. As bones contain large amounts of calcium carbonate, the combination of calcium carbonate with glycerine seems to work well and the glycerine may help to make the combination less brittle.

In tests it was found that the addition of glycerine did not necessarily reduce the brittleness of material mixes, but when mixed with eggshell powder and waterglass, the prints did have smoother surfaces. Whereas prints without glycerine felt rough and dry, prints with glycerine were much more smooth and almost felt soft to touch. When adding too much glycerine, it would reduce drying speed of the material mix and prints would collapse after they were finished.

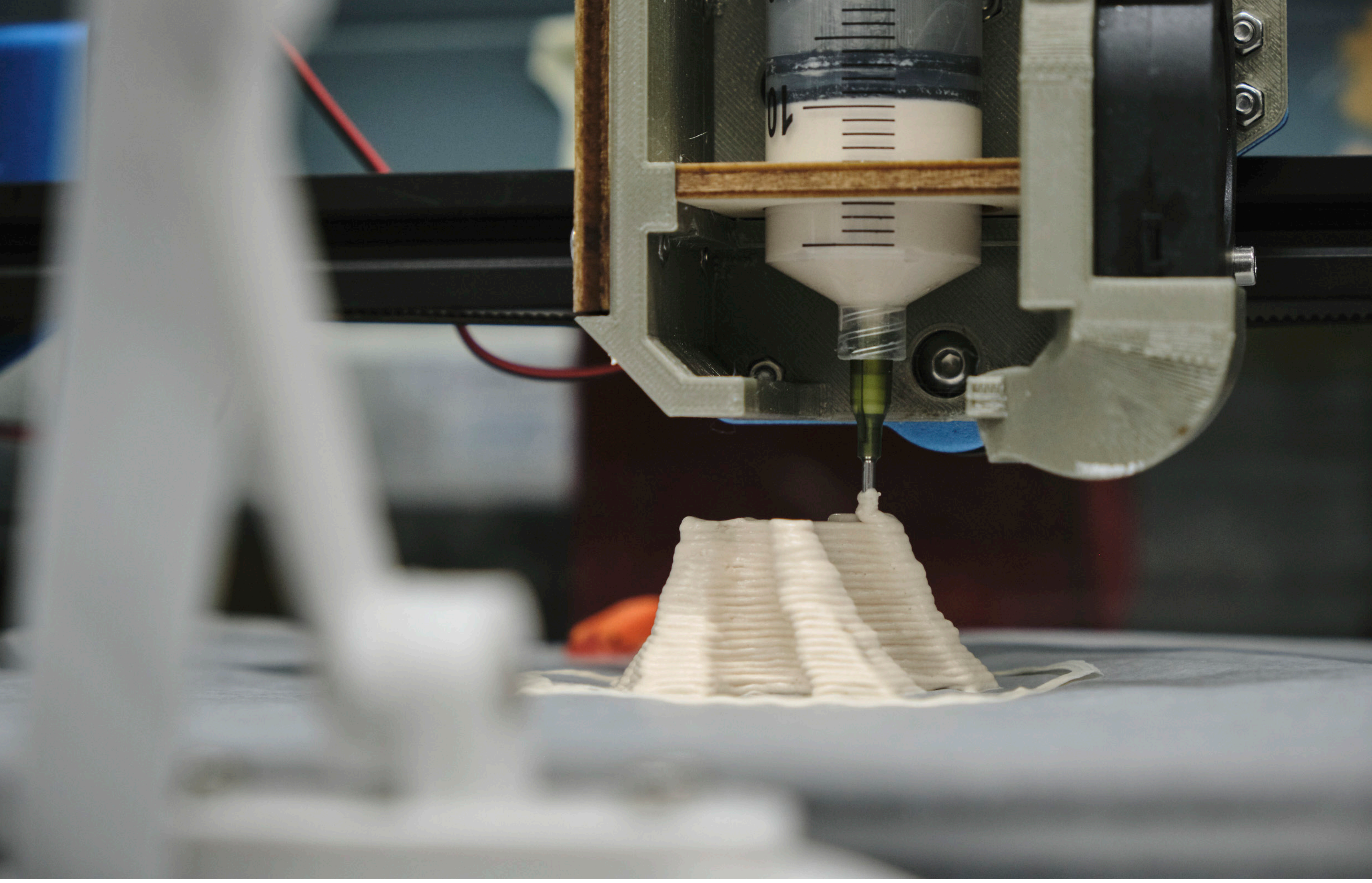


Figure 34: The final material mix

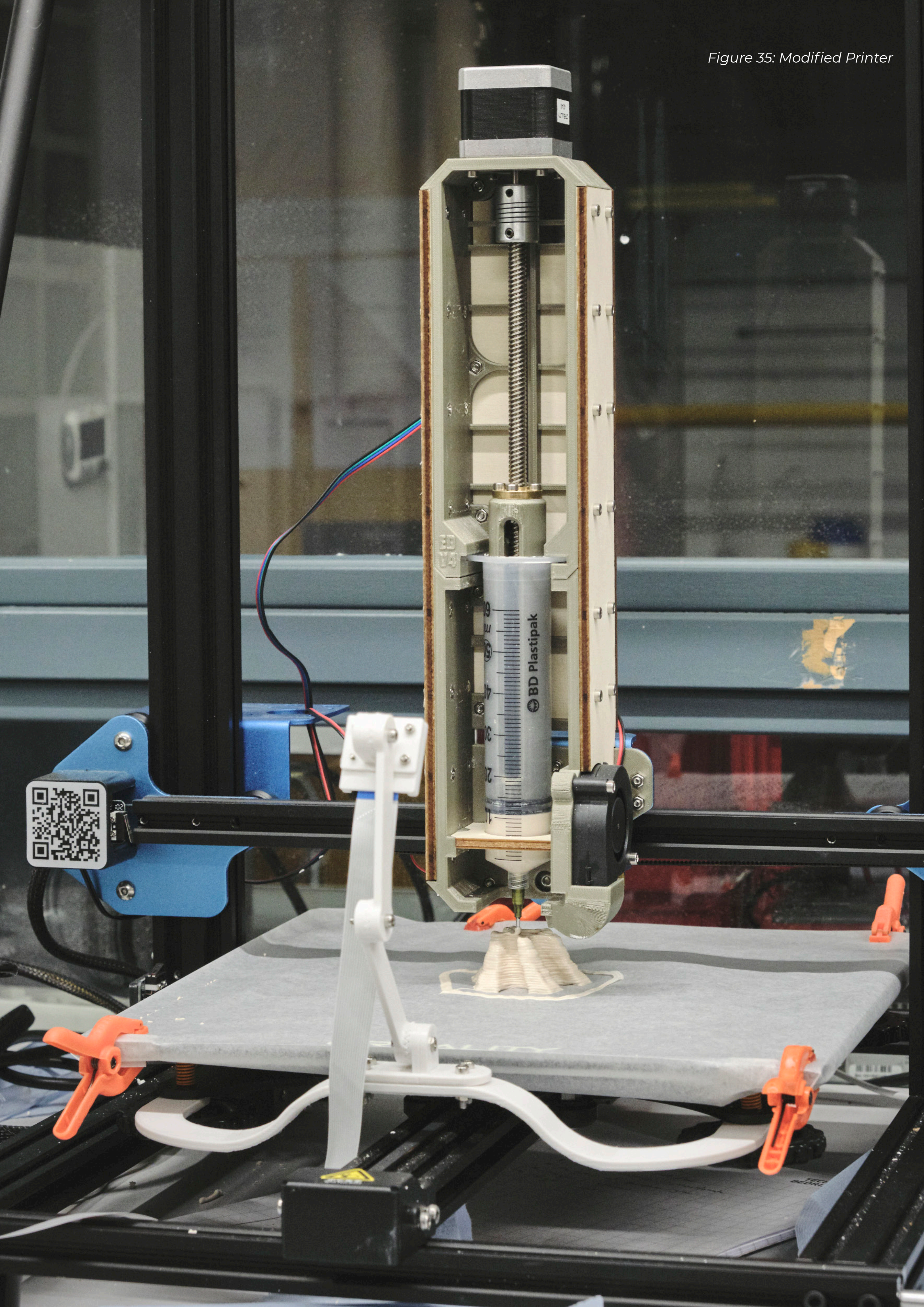
Final Material Mix Recipe

The final material mix recipe consists of a mixture of eggshell powder, waterglass and glycerol. The waterglass allowed the material mix to dry fast enough to provide support for the next layers, making it possible to print higher models and the glycerol provided the prints with a smooth texture, making them more pleasant to touch.

In tests, the material mix was made using 26.0 gram of eggshell powder, 16.0 gram of waterglass and 2.0 gram of glycerine, equating to a ratio of 59.1% eggshell powder, 36.4% waterglass and 4.5% glycerine.

The resulting prints dry fast enough to support additional layers so higher models can be made. Thin-walled models dry fast enough to be touched and picked up right after the print has finished, while prints with larger, dense volumes, will need a few hours or even days to fully dry. Due to the addition of glycerine, the texture is quite smooth, but a grainy texture is still noticeable. The mixture is also quite brittle and can be broken by hand, although it does require a reasonable amount of force.

Figure 35: Modified Printer



Ch. 7 | Printing Procedure

Printing with pastes is still in its infancy. More and more research into printing with paste-like materials is being done in attempts to make AM more sustainable, but as everything is still in early development phases, there are no clear procedures yet for the printing process. During the project it was found that print settings were hugely influencial on the printing results. This chapter will describe the procedures that have been developed throughout this project through testing different approaches.

The order of steps that was taken during the project was often to prepare the G-code and load them onto the printer, prepare the printer by cleaning it and placing the baking paper or plastic sheet onto the printbed and then prepare the material mix and loading it onto the syringe. The time that it takes to place the baking paper and to prepare the G-code could mean that material inside the needle/nozzle would dry, clogging the printer. This was fixable by removing the material with a nail or pin, but fully preparing the printer before making and loading the material seemed like the more efficient approach. The process of developing material mixes has been discussed in previous chapters. Here the preparation of the G-code as well as the best way to load material mix into the syringe will be discussed.

Preparing the G-code

The first step of starting a new print is to prepare the G-code. Ultimaker's Cura was used for slicing and generating G-code.

G-code preparation has been an iterative process in which several parameters were changed one by one to see their effect on the printing results. For several material mixes improvements of the printing results could be made by altering the settings. For example, differences in viscosity of the material mix seemed to require different settings for the print. All parameters were altered directly in Cura and no modifications of the G-code were made afterwards.

However, in Cura, the plugin 'Printer Settings' by fieldOfView was used. Whereas Cura itself only allows selection of conventional FDM nozzle sizes (0.2, 0.3 0.4, 0.5, 0.6, 0.8, 1.0), the plugin allows any value to be filled in. As the nozzle size is directly related to the linewidth, and the needle sizes that were used substantially differ from the conventional FDM nozzle sizes, full control over the value was essential. The plugin also allows one to fill in the outside diameter of the nozzle as well as the lowest point of the printhead (compared to the nozzle) in order to prevent any collisions between printhead and print.

A link to download all Cura profiles can be found in Appendix G.

Slicing settings

In this section the settings will be discussed that have been vital in getting good printing results.

(Initial) Layer Height

As the name suggests, layer height is the height at which each layer is printed. In conventional FDM, the recommended layer height is between 25% and 80% of the nozzle size. The layer height could be seen as the resolution in the Z-direction: a smaller layer height, or higher resolution in the Z-direction, means a smoother surface as the larger amount of layers are better able to show subtle differences in volume-change. The downside of a lower layerheight is that prints take longer as more layers have to be printed. During most tests in the project, layer heights that were 80% of the nozzle size, have been used in order to create more volume fast. However, in personal contact dr. Faludi mentioned that former students of his used layer heights that were roughly 50% of the nozzle size for the printing of paste-like material mixes and VormVrij's Yao van den Heerik mentioned that they usually use a layer height that is 33% of the nozzle size for the printing of clay.

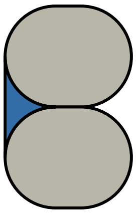
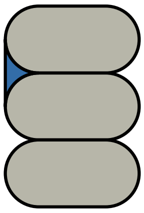
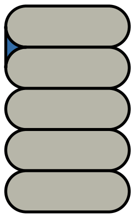
Visual			
Layer Height	*1.2 mm*	*0.75mm*	*0.5mm*
% of nozzle size	*80%*	*50%*	*33%*
Notch Height	*1.2mm*	*0.75mm*	*0.5mm*
Notch Depth	*0.6mm*	*0.375mm*	*0.25mm*
Notch Area (blue)	*0.15mm^2*	*0.06mm^2*	*0.3mm^2*

Table 3: Relation between layer height and notch size

There are two more important considerations in choosing layer height when surface smoothness is a consideration: notch size and print line rolling.

First, when choosing higher layer heights, the printed lines get squished down less, meaning that the lines remain relatively round. As a result of that, the prints surface have larger notches between the layers. Table 3 shows a comparison between using layer heights that are 80%, 50% and 33% of the nozzle size. As can be seen, with smaller layer heights, more layers are required to get to a similar height, but the notches also get smaller. Notches are shown in blue. Their height is the same as the layer height and notch depth is 50% of the layer height. The notch area can be calculated as follows:

$\text{Notch area} = 0.5 * \text{layer height} - 1/2 * \text{Pi} * (\text{layerheight} / 2)^2$

The quadratic relation between layer height and notch area shows how big the impact of layer height can be. Thus, if smoother surfaces are desired, layer height should be lowered.

The other consideration has also got to do with the relatively round crosssection of the printing line, which seemed to have been one of the main causes of wobbliness in a lot of prints that have been made throughout the project. The more round the crosssection of a line is, the more likely it is to roll, especially when the surface underneath is also round. Figure 36 shows the rolling behaviour for layer heights that are relatively high when compared to the nozzle size (and thus line width). It is importan to realize that figure 35 shows the perfect situation where lines are perfectly symetrical and the layers are all in one vertical, while in reality this will hardly ever

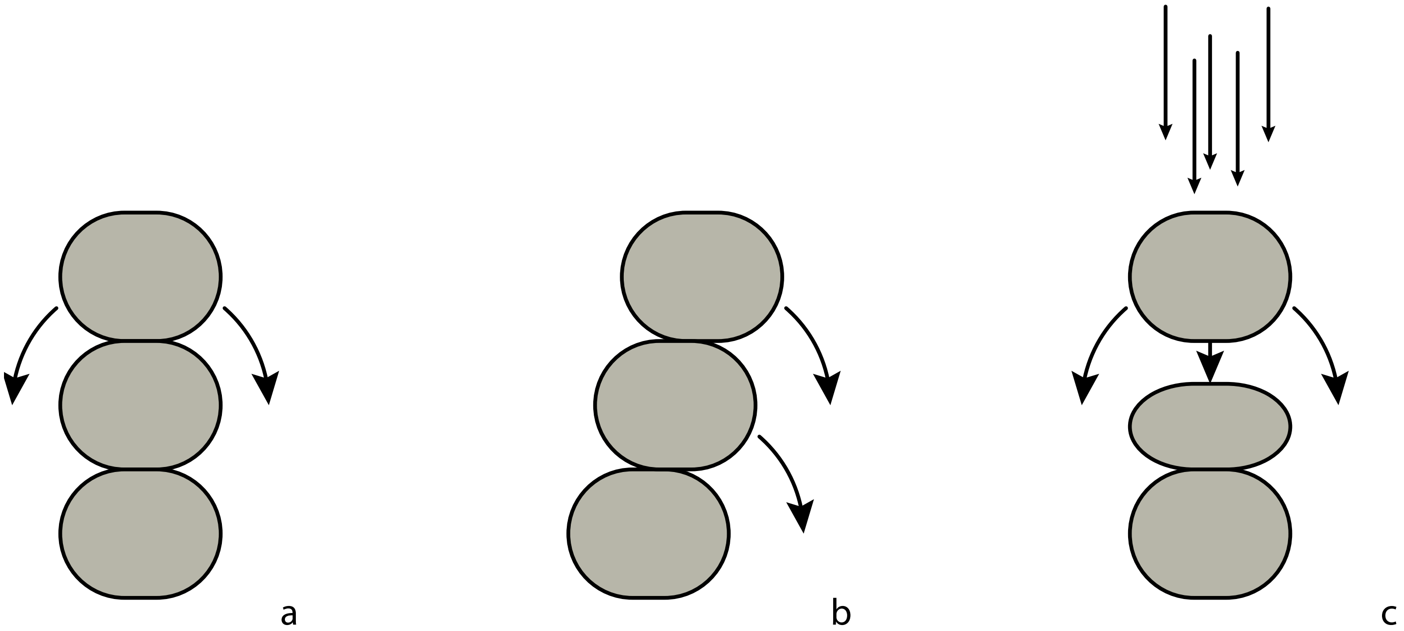


Figure 36: Rolling behaviour in relatively high layer heights; a - ideal situation, b - situation for overhang, c - situation for extrusion inconsistencies

be the case. In reality, there will likely be some overhang, offsetting some of the lines to either side, further encouraging the rolling behaviour. On top of that, due to inconsistencies in extrusion, it will sometimes be the case that the layers below are not as high as the printer expects and extruded material is dropped onto the lower layer, also making rolling more likely to happen. Again, the rolling behaviour can be prevented to some extend by choosing a relatively low layer height, but this will mean that the print will take longer to finish and, as the nozzle is pressed against the material more, the risk of the nozzle clogging due to material drying inside, is also increased.

Line Width

Line width is identical to the nozzle size. The process of selecting a nozzle size, and some of the implications that come with that have been discussed in Chapter 3. Here the topic will be further discussed. While layer height can be seen as the determining factor of resolution in the Z-diretion, line width is the determining factor of resolution in the X- and Y-direction. The smaller the line width, the more lines are necessary to fill in all volume in one layer and the more detail can be achieved. Especially corners can be made sharper with smaller line width as compared to larger line widths, see figure 37. The blue area is the desired print surface, while the grey lines represent what is actually printed. The sharpest corners will still have a rounding equal to 50% of the line width. The sharper the corner, the more substantial the part that is removed due to rounding, which can be seen in the larger blue areas that become visible.

Also, cornering leads to small cavities in between the print lines where no material is deposited. In conventional FDM printing, these cavities are generally hardly noticeable due the small size of the nozzles that are used. And, again, like with smaller layer heights, having smaller line widths also means that it will take longer to finish the prints, as more lines will need to be printed to fill in the same volume. Furthermore, as a smaller line width requires a smaller nozzle, the risk of the nozzle clogging is also increased as the material inside will solidify faster.

Infill Density

Whereas with conventional FDM, infill densities can be lowered in order to lower material use, while still retaining decent mechanical properties, for printing with paste this is a lot more difficult.

Infill in conventional FDM is possible because extruded filament solidifies virtually instantaneously so a decent amount of overhang and bridging is possible. This ability to do bridging and considerable amount of overhang are important enablers of having infill. The paste-like material mixes that have been tested throughout the project require more time to solidy, limiting the amount of overhang that is possible and bridging has not been possible at all. This means that infill cannot be done cleanly and is mostly ruled out as a changeable parameter. Some testing with infill has been done, but for most prints infill has been set to 100%.

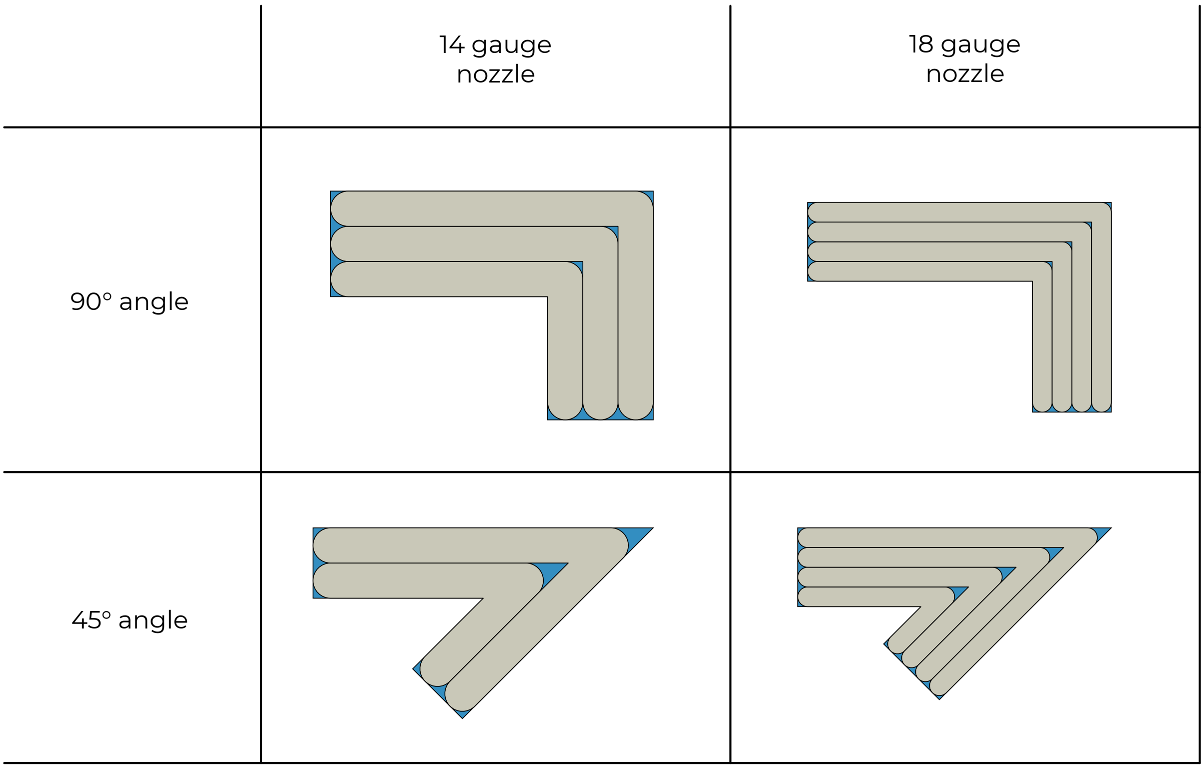
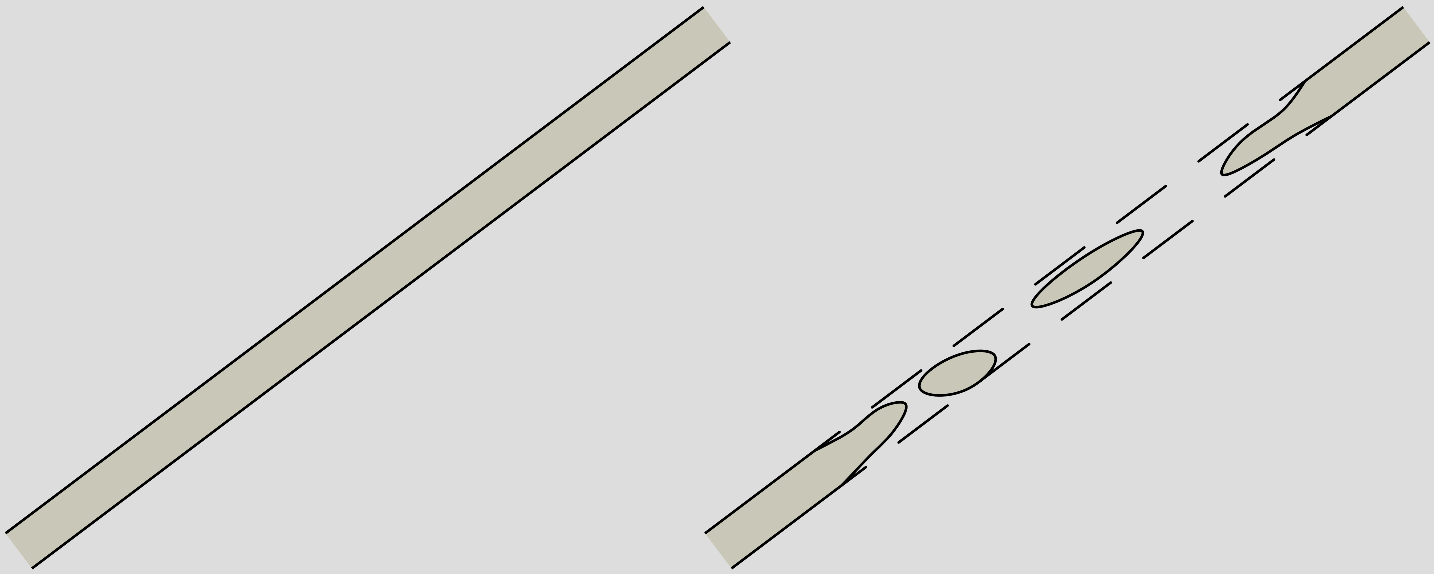


Figure 37: Line width vs corner sharpness (blue is desired surface area)



a | Speed good

b | Speed too high, leading to inconsistent extrusion (dashed line is desired print line)

Figure 38: Effect print speed

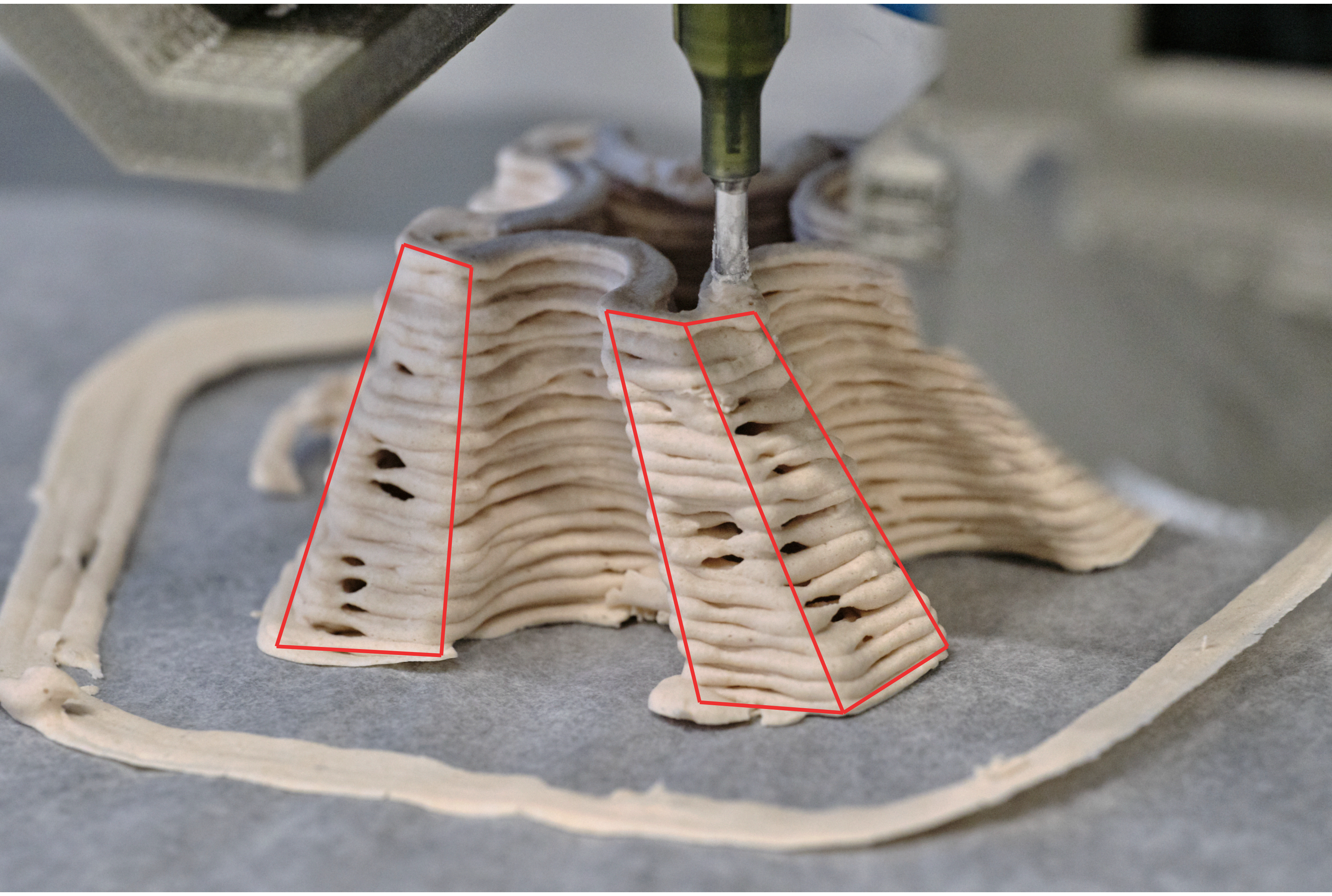


Figure 39: Porosity in print due to high print speed. Lines inside red outlined areas are all straight

Figure 40: High Travel Speed Damaging Prints

Flow

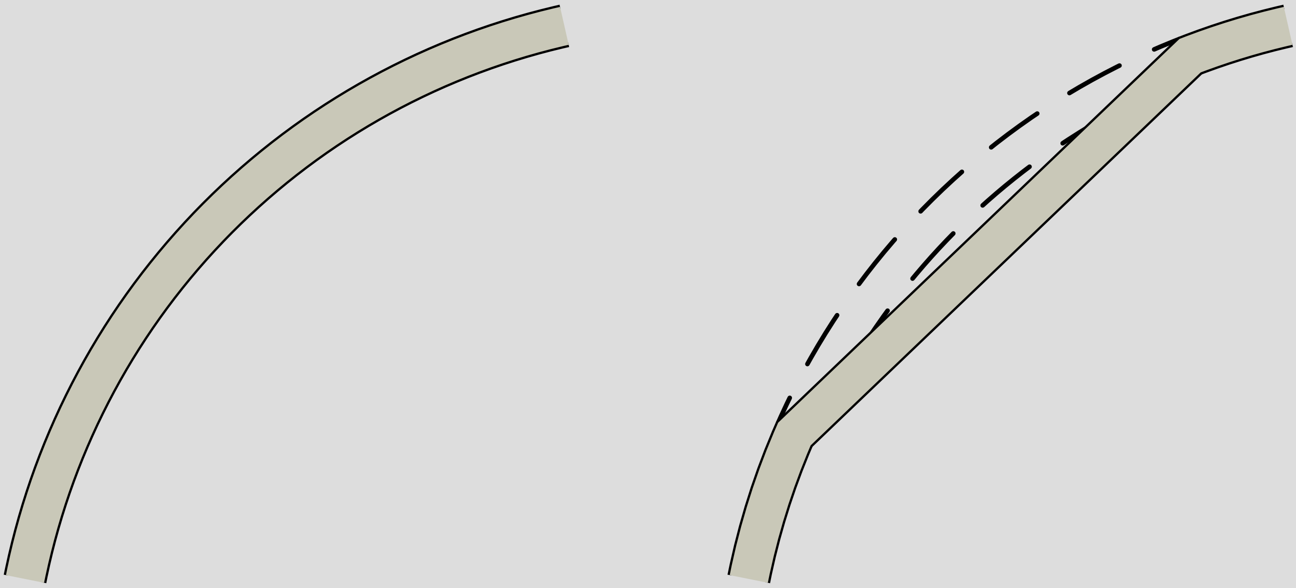
In tests it was found that different flow rates were needed for the different material mixes that were made. The most suitable flow rate seems to depend on the viscosity of the material mix that is printed with. As mentioned in Chapter 3, speed of the extrusion motor was adjusted in the Marlin firmware, allowing more easy control over the flowrate while slicing models. In practice, less viscous materials seemed to require a lower flow rate as they ‘flow‘ more easily from the syringe. More viscous material mixes require a higher flow rate to be extruded properly. However, the calculations that were made for adjusting the extrusion motor speed in Marlin (Chapter 3) already seemed to have been quite accurate, which makes sense as volume change in the syringe, which was calculated, should theoretically match the amount of material that is extruded.

Print Speed

Due to shear thinning behaviour of the material mixes, the print speeds had to be lowered considerably. With higher print speeds, part of the model not be printed as the varations in viscosity prevent consistent extrusion. For example, if a straight line were to be printed, it would likely be the case that part of the beginning of that line will be missing as the higher viscosity of the material mix would result in a lack of of extrusion. While default print speed for conventional FDM is set at 60mm/s, the printspeed for printing with paste is often less than 25% of that. Logically, this would mean that prints take a lot longer to be made. However, as the nozzle size is often larger than the ones commonly used for conventional FDM, the same volume can be created with less lines. As a result of that, the slower print speed is (partially) compensated. However, the lower the printspeed, the more accurate the print will likely be, as shear thinning behaviour gets eliminated. The downside will be the longer printing time. These considerations will have to be made when selecting the print speed.

Travel Speed

Travel speed is the speed of the printhead moving while no extrusion is being done. For traveling that is done outside of the xy-surface of the print, speed does not matter and can be as high as the printer can support. Part of the traveling however is done while the nozzle is above the xy-surface of the print. During some prints, where travel speed was set to the default Cura value, the nozzle would move through the freshly extruded material mix that was still solidifying, moving it aside, causing deformations in the print. In some cases the material mix had already dried when the nozzle traveled over it at high speed, causing parts of the print to break off, see figure 40. Especially when a bit of material was dried on the side of the nozzle it



a | Accelaration good

b | Accelaration too high (dashed line is desired curve)

Figure 41: Effect print accelaration

could cause a lot of damage to the print. Therefore, it is recommended to start working with low travel speeds and increase it step by step if the material mix allows it. The default travel speed in Cura (for conventional FDM printing) is 150mm/s, but for most tests in printing with paste-like material mixes, the speed was set at only 10% of that or even less.

Print Acceleration

Whereas Print Speed controls the speed in a straight line, Print Accelaration mostly influences how fast curves and corners are being printed, thus when direction changes. If acceleration is set too high, extruded material mix does not adhere well to the printbed or layer below and instead is dragged behind the nozzle until gravity takes hold of it and it is dropped in a random location. However, setting the Print Acceleration too low, it will likely lead to overextrusion due to shear thinning behaviour of the material mix. This can especially be witnessed at sharper corners. The extreme direction change at sharp corners will result in the printhead standing still momentarily. The lower the Print Acceleration, the longer this takes. During this brief pause, shear thinning behaviour of the material mix will have extrusion continue, resulting in overextrusion. Instead of a sharp corner, there will be a small blob of material.

Print Jerk

Due to the delayed response in extrusion caused by sheer thinning behaviour of the material mix, extrusion cannot start and stop instantaneously. At sharp corners, where acceleration reaches its most extreme values, this can result in overextrusion that form round blobs, see figure 42. Whereas print accelaration influences all accelaration, from slight curves to sharp corners, print jerk only influences how fast the nozzle moves around (sharp) corners. So while Print Acceleration may have to be set at a lower value in order to allow sufficient adhesion between individual layers and/or the printbed, Print Jerk may have to be increased in order to prevent overextrusion at (sharp) corners so they can keep their crispness.

Print Cooling

As mentioned in chapter Chapter 3, for the first few versions of the printer modification, the addition of a cooling fan was omitted as it was assumed that cooling would not be necessary considering no heat was added while printing. Based on recommendations in later versions a few was added, helping to speed up the solidification process of some of the material mixes that have been tested.

Cura allows users to select maximum fan speed as well as the starting point and build-up of turning on the fan. During tests it was found that using fans in a similar way as they're used in conventional FDM seems most effective.

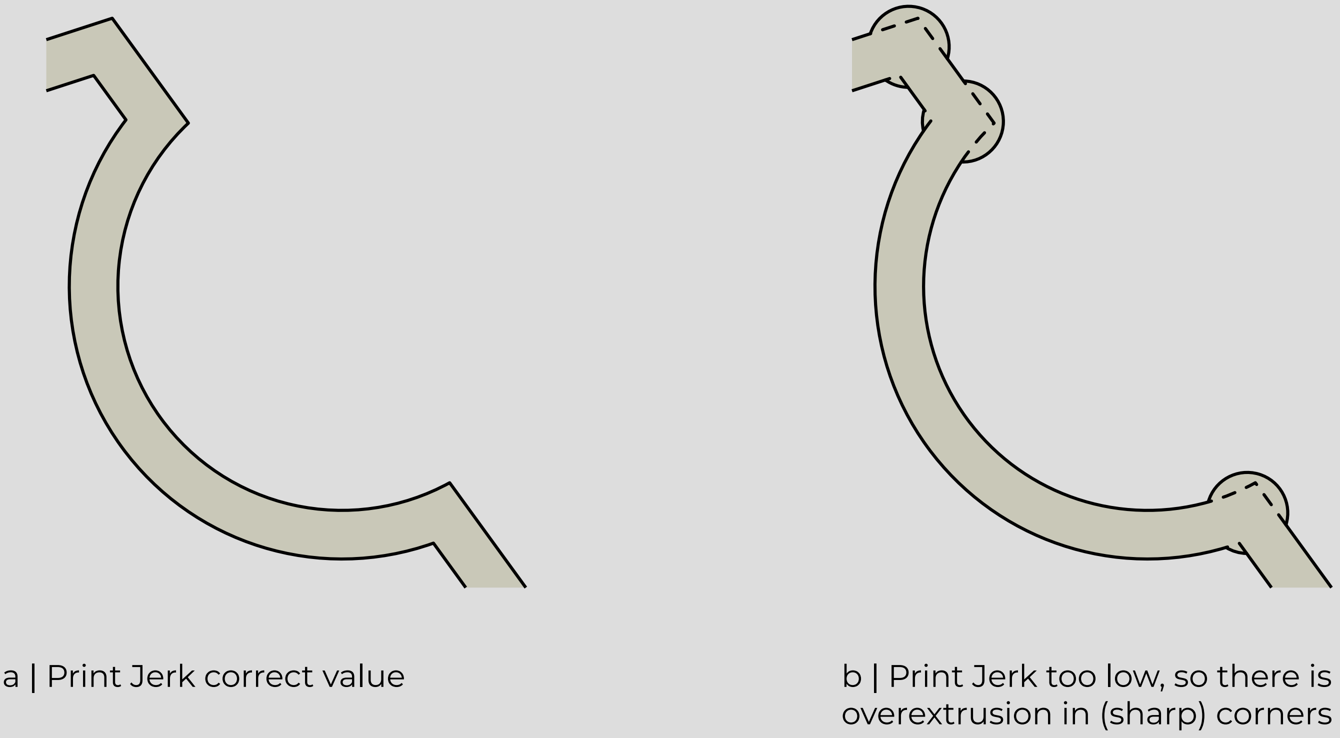


Figure 42: Overextrusion issues at (sharp) corners can be solved with Print Jerk

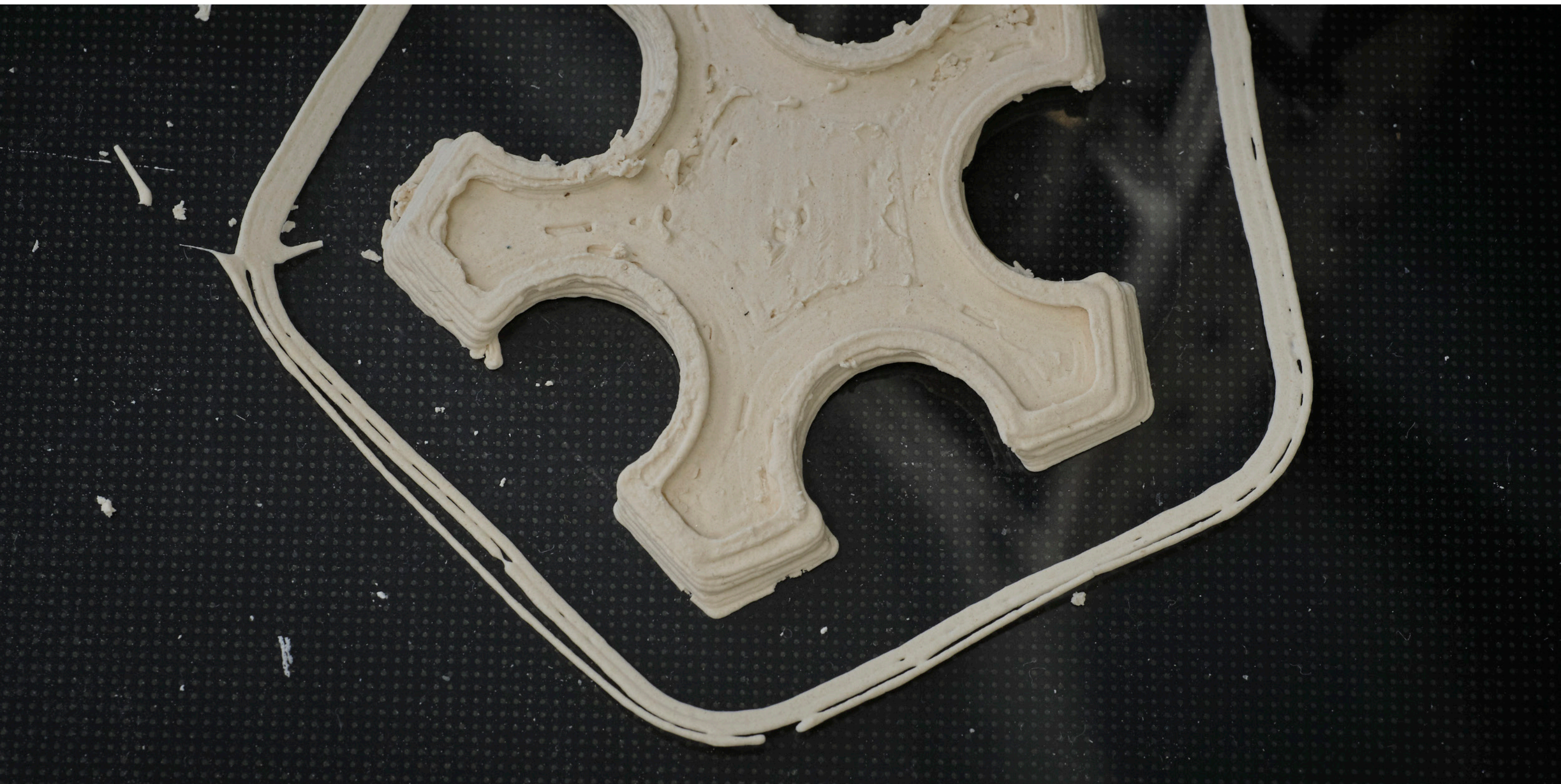
Skirt

Printing a skirt has been a extremely useful tool to make sure flow is fairly consistent when doing a print. The purge line, that in conventional FDM printing is used to ensure good extrusion, didn't work well in tests with printing with paste-like material mixes. Although some material was extruded, it wasn't a clean line, like normally is the case for conventional FDM printing. The process of printing a skirt however, did help to ensure good and fairly consistent extrusion. If skirts were disabled, the first layer of the model often had inconsistencies which resulted in defects in the print or the print failing fully.

Spiralize

Turning on spiralize mode in Cura can be a way to improve surface quality on prints. When spiralize mode is turned off, the printer stops printing in between layer changes, resulting in small gaps where lines are started and ended. In conventional 3D printing this gap is barely visible as the line width is small, extrusion is consistent and the slicer tries to change layers in a less visible location, obscuring the layer change. When printing

Figure 43: Extrusion gradually get more conistent while printing skirt



with paste-like material mixes, the layer change location is often more clearly visible as larger nozzle sizes are being used and sheer thinning behaviour of the material often causes a small delay in extrusion, resulting in bigger gaps where lines start and end. By turning on spiralize mode, the model will be printed in one continuous line, eliminating the gaps at layer change locations.

Preparing the printer

Cleaning the printer

Making sure that the printer and printbed are clean as any dried material can lead to printfailure as the dried material may impede smooth movement of the printer or extrusion, which could cause the nozzle to clog, the print to get damaged or the material on the printbed (baking paper or plastic sheet) to be damaged. As prints were normally performed on top of said baking paper or plastic sheet, the printer normally did not get dirty, but still it needs to be checked. Cleaning was done using tissuepaper and isopropanol.

Placing baking paper or plastic sheet

Next the baking paper or plastic sheet is placed on the printbed and pinned down using clamps. As mentioned in chapter 3, the baking paper and plastic sheet are an easy way to make sure the print does not get stuck to the printbed itself and can be removed without damaging either the print or the printbed.

Uploading G-code

The next step in preparing the printer is to load the G-code onto the printer itself, or, as was the case for most of this project, into OctoPi.

(Check) Calibration of the printer

The last step in preparing the printer is to check whether the calibration of the printer is correct. To do this, the empty syringe with nozzle attached should be placed in the printer and a regular sheet of paper should be placed on the printbed. When moving the printhead around the printbed at a height of 0 on the Z-axis, the nozzle should just be lightly touching the paper. The friction should neither scratch nor move the paper. The fact that the luer lock nozzle is screwed onto the syringe, make it sensitive to deviations in nozzle height as the nozzle is likely to be screwed in different amounts every time. If possible it is reommmended to keep the nozzle on after calibration, in order to prevent printfailure due to inaccurate calibration.

Loading the printer

After the G-code has been prepared and is uploaded to OctoPi (or loaded to the SD-card in the printer), the printer has been cleaned and baking paper or plastic sheet has been placed on the print bed, the material mix can be prepared and loaded onto the printer. The process of preparing the material mix has been discussed in Chapter 4. Here the process of loading the mix onto the printer will be described.

Adding materials to the syringe

When loading the syringe, it is important to have as little air in there as possible. Air bubbles in the material cause inconsistencies in extrusion, which in turn leads to defects in the prints, such as porosity, or could result in (part of) the print collapsing. When larger quantities of material is available, the syringe can be filled by wiping the material over the entrance of the syringe, while making sure no air pockets are created, see figures 44 to 46.

Another approach to prevent air bubbles in a syringe, that works best with less viscous materials is to hold the syringe upside down and slowly press the plunger down. Gravity will force the material down against the plunger and air will be pressed out of the syringe first. By continuously pressing onto the plunger until material starts to come out of the nozzle, it possible to remove (most of) the air from the syringe, making sure that the extrusion will be as consistent as possible. This solution is standard procedure in healthcare when injecting a patient, as air bubbles could cause heart attacks, respiratory failure, strokes or air embolisms and thus potentially even kill the injected.

Test extrusion

Once the syringe, filled with material mix, has been succesfully mounted onto the printer, it is necessary to test extrusion before any print can be made. If extrusion doesn’t start out conistent in the print, it may lead to the print failing. Extrusion can be tested in the interface of the printer itself or in OctoPi. By moving the extrusion motor little by little, material should start to pour out of the nozzle. At the point where every time the extrusion motor is moved, material flows out of the nozzle, it can be expected that extrusion in the print will also start out fine.

Figure 44, 45 & 46: Steps for properly filling a syringe

Figure 47: Extrusion may not start out well

Running the print

Start print

Once all the previous steps have been completed, the print can be started. When the print has been started, the printer will first home all axes and start printing the purge line. As the homing point is actually slightly off to the side of the printbed, it is important to make sure that the nozzle moves smoothly over the baking paper or plastic sheet that has been placed on top of the print bed. If the baking paper or plastic sheet has not been placed completely flat on top of the print bed, the nozzle might jam into the side of it, which could lead to several issues, depending on the print bed cover that is used. In case baking paper has been applied, the paper is likely to get torn. If a plastic sheet is applied, the sheet could be pushed off, the sheet could get scratched by the nozzle or the nozzle could even get buckled due to the force of the stepper motors jamming the nozzle into the plastic sheet.

After homing all axes and moving the nozzle over the printbed, the printer will start to print a purge line on the side of the printbed. During all tests, the purge line would not print well, but it would still be useful to start up extrusion. During the purge line it will make a back and forth movement while continuously extruding. Material that is extruded during the ‘forth‘ movement could get stuck to the nozzle during the ‘back‘ movement. Usually this clump would get dislodged while printing the skirt around the model, and thus shouldn’t pose any risk for the model, but manually removing it using tweezers has been found to be the safest approach, as it is the most sure way to remove any clumps.

Trouble shooting while printing

Ideally, the printing process should run free from issues. During tests this was not always the case. If all printing settings are correct, the material should solidify in an appropriate amount of time, extrusion inconsistencies should be only minor and the nozzle shouldn’t get clogged. It is still good to monitor the quality of the print and remove any clumps that are formed using tweezers. In thin-walled prints this was generally not necessary, but for prints with larger volumes, such as cubes, there was a larger tendency for clumps being created.

Figure 48: Printing of bending specimens

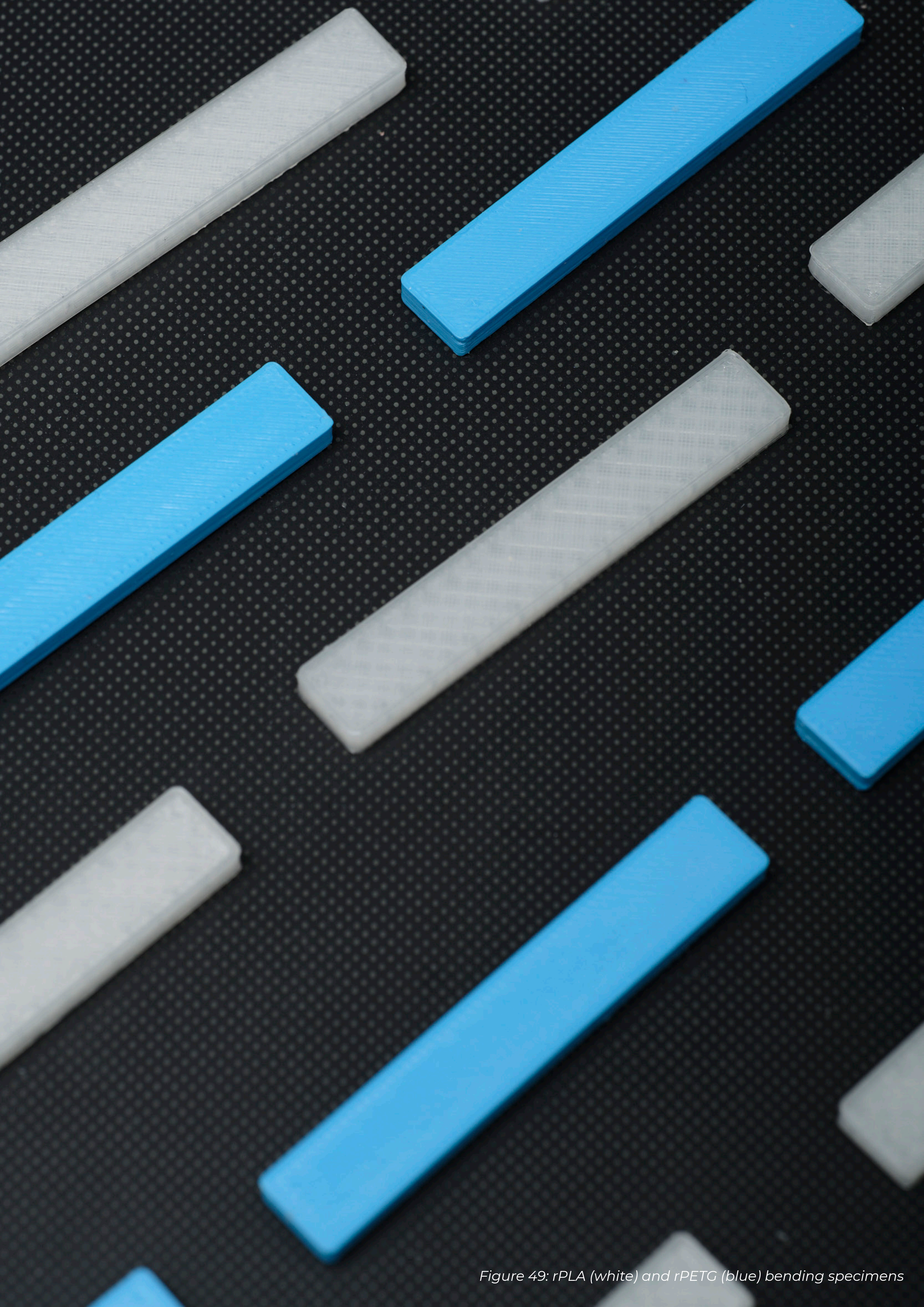


Figure 49: rPLA (white) and rPETG (blue) bending specimens

Ch. 8 | Results & Discussion

In previous chapters the process of developing a material mix has been described and one material mix has been chosen that gave the most promising results. In this chapter the found material mix will be further discussed and judged on the criteria that had been determined initially. Prints made with the material mix will be compared to ones made with rPLA and rPETG, two of the more sustainable filaments that are currently available.

Prints that were made using Reflow's rPLA and rPETG were printed on a Prusa i3 MK3S+ with a spring steel sheet (printbed) with smooth PEI coating. All rPLA and rPETG prints were made with a brim and hairspray applied to the printbed. Print bed adhesion was found to be poor without the use of hairspray. At first the poor bed adhesion was considered to be caused by poor printer calibration, but, as other filaments printed well, it was concluded that the poor bed adhesion was caused by the filament itself. The layer height of all rPLA and rPETG prints was set at 0.20mm, which should give the prints better mechanical properties than prints with a smaller layer height.

Criteria Assessment

Print-ability

The print-ability of the material mix will be assessed based on four different criteria: the material mix's ability to extrude, its ability to provide self-support, its ability to start and stop cleanly and finally the printing time.

Ability to extrude

The ability to extrude the material mix was found to be decent. It does require some preparation and tinkering to get consistent extrusion. Enabling the printing of a skirt was found vital in this. There were a few factors that could negatively impact the material mix's ability to extrude.

First, it happened frequently that small amounts of material mix would collect around the tip of the nozzle. Due to the relatively large surface area of these clumps and the fact that the fan would blow directly at them, they would often dry fairly fast and could then cause damage to the print that was being made. The dried clump would move through the still wet material that was just extruded, pushing it aside, potentially causing substantial damage. This issue was most often found when printin models that had larger volumes, such as cubes. In thin-walled models, such as the vase model, the issue was seen a lot less. Probably this is because the thin walled items are able to dry faster, making it less sensitive, and, in the thin-walled vase model, movement was always in the same direction, so the top layer was kept more flat. The clumps that collected around the nozzle could be picked away using tweezers, preventing a lot of damage, but at the same requiring a lot of supervision, which is undesirable.

Another factor that could negatively impact the material mixes ability to extrude is the nozzle's susceptibility to clog. Once the nozzle gets clogged, no material is getting extruded anymore and it's unlikely that the print can be saved. From tests, several factors were determined that lead to increased risk of the nozzle clogging.

1. The first factor is the nozzle size: smaller nozzles are more likely to get clogged. Only a small amount of material is needed to clog the nozzle, so this could be a reason to choose a larger nozzle for printing.
2. The second factor is print speed. If the print speed is set too low, material moves through the nozzle too slow, making it more likely to solidify inside the nozzle and thus clogging it. So print speed has to be low enough for the material to adhere well to the printbed or another layer, but high enough to prevent material from solidifying inside the nozzle.
3. The third factor is the layer height. When lower layer heights are used, the nozzle will press down more onto the line that is

extruded. In doing this, the nozzle may get encapsulated in the material, increasing the risk of it getting clogged. Increasing the print speed seems to be a solution for this, as it will make sure material keeps flowing.

Self-support

The ability to provide self-support is strongly dependent on the drying rate of the material mix. If the material mix does not dry sufficiently in between layers, there will not be enough stiffness to provide self-support. Most material mixes that were created throughout the project did not dry fast enough to be able to build much height. Even shapes as simple as a plain cube could not be printed well and a lot of models would start sagging during or after the printing process. The final material mix does dry fast enough due to the help of the added fan. Heights of several centimeter were succesfully achieved, but no prints bigger than 8 centimeter were ever attempted to be made.

Starting & Stopping Cleanly

The material mix is generally able to stop and start cleanly. It was found necessary to enable the printing of a skirt with each print in order to make sure that extrusion is consistent. The purge line that is printed at the start of each print was not found to be beneficial for the printing results and could even harm prints as the back and forth movement would often result in small amounts of material mix to collect around the nozzle. The slow and steady movement of the skirt around the model does help to improve consistency of the extrusion. In many prints, the skirt would start out as a inconsistent drooping of material or thin line, but as it got closer to finishing the skirt, it would turn out in a flat line, corresponding with the settings for line width and layer height.

Due to sheer thinning behaviour of the material mix, no abrupt changes in printing speed can be made. Starting and stopping (and any direction changes) have to be done slowly and deliberately, in order to make sure there is no over- or underextrusion.

Printing Time

Printing time is found to be highly dependent on the size of the nozzle that is used. For larger nozzles, line width and (often) layer height are larger, allowing volumes to be created with less movements, which results in a faster printing time. A direct comparison with conventional FDM printing is made difficult due to the difference in nozzle size that is suitable for use. As a result of the larger nozzle size, less detail can be achieved and subtle changes in surface direction may not be as noticable.

Conventional FDM printing is usually done with 0.4mm nozzles. The Reflow rPLA and rPETG filaments require a slightly slower printing speed compared to regular, ‘virgin‘ filaments. Printing of the vase model required around 3 hours and 30 minutes. In printing with paste, print time highly depends on the used nozzle size. For the same vase model, the print takes 2 hours and 25 minutes when the 1.50mm nozzle is used at a layer height of 0.75mm (50% of the nozzle size), while it would take 4 hours and 31 minutes if a 0.84mm nozzle is used at a layer height of 0.42mm (50% of the nozzle size).

While printing can be done in a similar or faster time if a larger nozzle or if relatively high layer height is chosen, but solidification of the material mix also takes substantially longer compared to the reference materials and other (plastic) filaments. Due to the fast cooling, conventianal (plastic) filaments solidify almost instantaneously and prints can be touched and used directly after the print is finished. In printing with the developed material mix, solidification depends on the geometry of the model. Thin-walled objects, such as the vase model, solidify fast enough to make it possible to touch and pick up the model directly after the print has finished. Models with highly dense volumes take considerably longer to dry. The bend specimens, which are beams of 58.4mm by 9.90mm by 4.00mm with 100% infill, took more than 24 hours to fully solidify. Drying time should thus be considered when printing models with large, fully dense volumes. The bending specimens were relatively small, so larger models could potentially take several days to fully solidify.

Dimensional Accuracy

Matching CAD model dimension

Several specimens were printed for a bending test. These specimens had the shape of a elongated beam. Measurements of the CAD model were 58.4mm in length, 9.9mm in width and 4.00mm in height.

Table 4 shows the measurements that were made for the lenghts, widths and heights of the prints that were made with rPLA and rPETG from filament manufacturer ReFLow and the prints made with the material mix. Every measurement was taken three times and the values in the table represent the average of these measurements. As can be seen, dimensions of the rPLA and rPETG barely deviate from the CAD dimensions, with most differences being less than 0.4%. The largest deviation of the plastics is found in rPLA which deviates 1.31% from the CAD in height, which corresponds to the Z-direction in the print.

Prints made with the material mix deviated from the CAD dimensions a lot more, with the length (X-direction in print) being 1.68% smaller, the width (Y-direction in print) being 5.81% smaller and the height (Z-direction in print) being 4.79% smaller. It is interesting to see that the deviation in the X-direction is relatively low compared to the deviation in the Y- and Z-direction. As the models are build layer by layer, it would make more sense if the deviation in X- and Y-direction would have been more similar and the deviation in the Z-direction would have been the one that is different. All individual layers get some time to solidify, before the next layer is placed, so a more similar deviation in the X- and Y-direction was expected. The length of the model is substantially bigger than the width and height of the model, so perhaps this explains the relatively low percentual deviation. In actual distance, the deviation in length of the prints is clearly larger than the deviation in width and height.

It must be noted that the prints made with the material mix are somewhat wobbly which might be part of the reason why there is a larger devation in their dimensions when compared to the prints made with rPLA and rPETG. All measurements were done three times in order to decrease the chance of incorrect measurements, but the wobbliness could have resulted in repeated wrong

	rPLA	rPETG	Material Mix
Prints Measured	*11*	*6*	*7*
Length CAD (mm)	*58.40*	*58.40*	*58.40*
Length Print (mm)	*58.21*	*58.28*	*47.42*
Length Deviation (mm)	*-0.19*	*-0.12*	*-0.98*
Length Deviation (%)	*-0.32*	*-0.21*	*-1.68*
Height CAD (mm)	*4.00*	*4.00*	*4.00*
Height Print (mm)	*4.05*	*3.99*	*3.77*
Height Deviation (mm)	*0.05*	*-0.01*	*-0.23*
Height Deviation (%)	*1.31*	*-0.36*	*-5.81*
Width CAD (mm)	*9.90*	*9.90*	*9.90*
Width Print (mm)	*9.87*	*9.87*	*9.43*
Width Deviation (mm)	*-0.03*	*-0.03*	*-0.47*
Width Deviation (%)	*-0.31*	*-0.27*	*-4.79*

Table 4: Dimensionsal measurements and deviations

Table 50: Printing time depends strongly on nozzle size and print settings related to it

Figure 51: Warping of bending specimens suggested

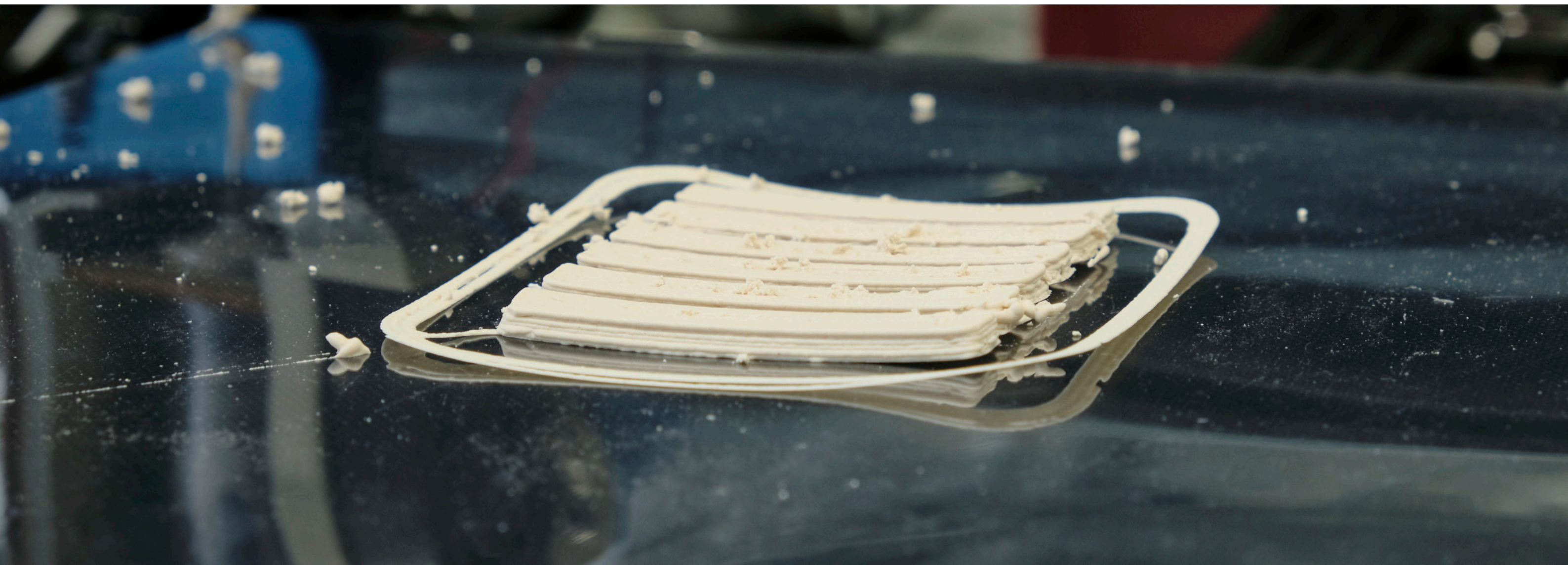
measurements due to the caliper being put in an angle. Considering all measurments are smaller than the theoretical dimensions rather than larger, it seems unlikely that the deviation is caused by wobbliness.

Shrinking or Warping

One of the main causes of shrinkage and warping are residual stresses in the material. In conventional FDM printing, these residual stresses are formed due to differential cooling of the printed part. As filaments are heated up in conventional FDM, prints are more prone to heat induced shrinkage and warping (Redwood, 2020). While printing with rPLA and rPETG, no noticable warping or shrinkage was witnessed. Parts were printed with a brim and hairspray was applied to the printbed in order to improve bed adhesion.

When printing with the material mixes, not heat was introduced and thus no heat induced shrinkage and warping should be possible. Shrinkage and warping as a result of differential solidification is possible however. In practice, no clear warping of models was witnessed. Any deformation of the print seemed to have been the result of printing and storing not fully dried prints on uneven surfaces. As discussed in Chapter 3, printing on baking paper caused a rippling effect on the bottom of the prints. The plastic sheet generally was a lot flatter and gave very flat bottom surfaces. The day after printing the aforementioned bending specimens, they seemed to have warped (figure 51), but it was then found that the plastic sheet had curled up slightly due to improper attachment to the printbed. After letting the models finish drying on a flat surface, the deformation had gone fully, suggesting it could not have been warping.

Figure 52: Clear warping of skirt around bending specimens



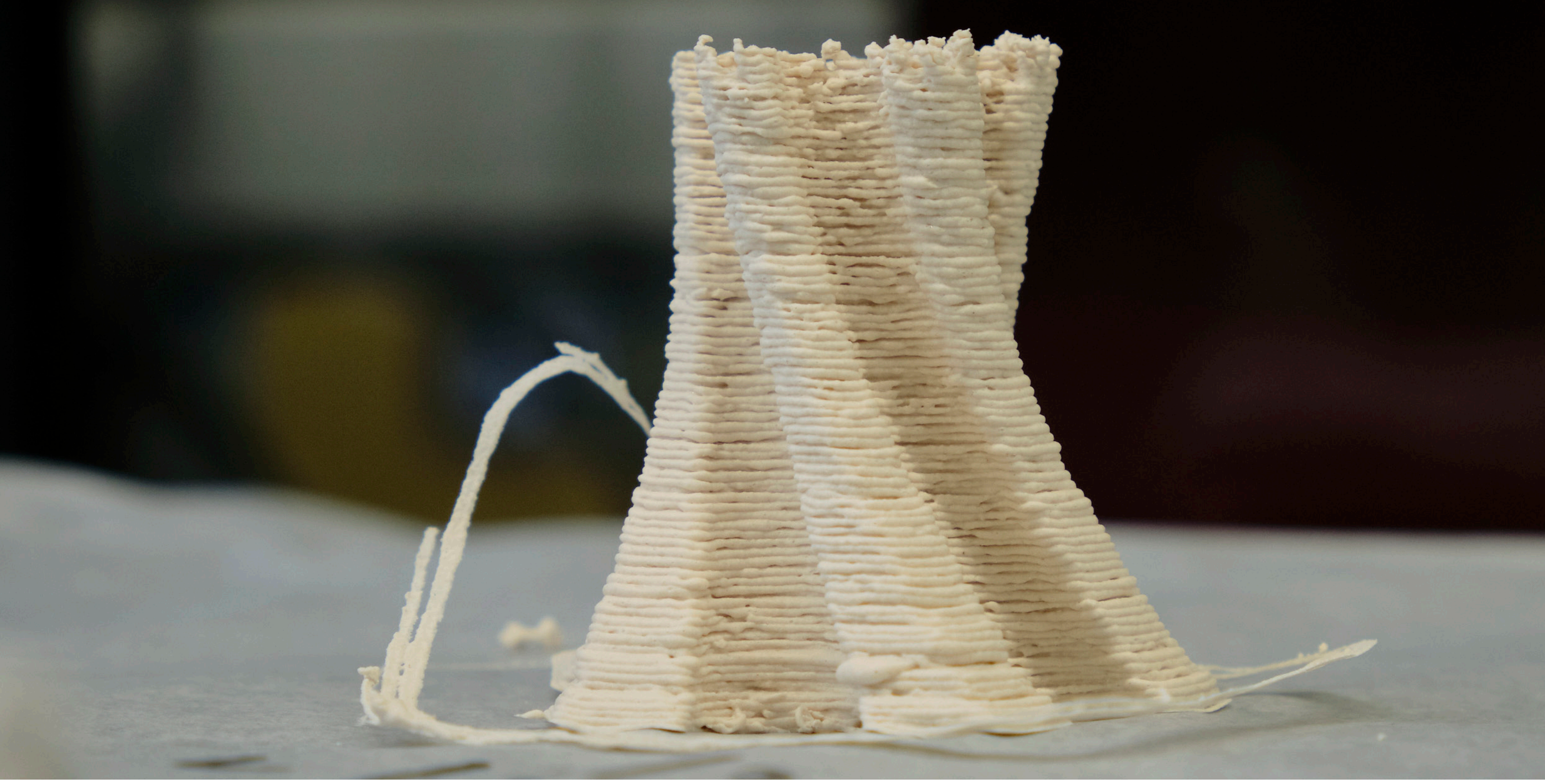


Figure 53 Lowering the layerheight increases resolution in the Z-direction

Skirts did warp substantially however, as deformation was substantially bigger than the baking paper or plastic sheet could have caused, see figure 52. The skirt is composed of only a single layer so it seems like the material does have a tendency to warp, but the weight of several layers above will press the material down enough to prevent any warping. Warping of the skirt should not pose any concern as it will likely be thrown away anyway.

Resolution

Resolution can be divided in two parts: resolution in the X- and Y-direction and resolution in the Z-direction.

Resolution in the X- and Y-direction depends on the linewidth and thus on the nozzle size. As described in Chapter 3, a smaller nozzle is better able to print small details, which is especially noticable at sharper corners and details. Larger nozzles will round off these corners with the nozzles radius. In tests it was possible to print succesfully with 18 gauge nozzles, which have a diameter of 0.84mm. This is of course substantially larger than the 0.4mm nozzles that are often used in conventional FDM printing. As a result of that, less detail can be achieved while printing with the material mix in comparison with prints made with the plastic filaments.

Resolution in the Z-direction depends on the layer height that is used. In conventional layer heights are between 0.05 and 0.4mm (Redwood, 2020) and the chosen value depends on the desired resolution and nozzle size used. Printer manufacturer Prusa recommends a maximum layer height of 80% of the nozzle size (Zuza, 2017), while 3D printing blog, 3D Printerly, recommends a layer height of between 25% and 75% of the nozzle size (Dwamena, 2022). As discussed in Chapter 3, layer heights of between 50% and 80% of the nozzle size have been tested. Prints made a relatively low layer height (i.e. closer to 50% of the nozzle size) had more smooth surfaces and were less wobbly, but were more likely to fail due to the nozzle getting clogged, whereas prints made with a relatively high layer height (i.e. closer to 80% of the nozzle size) were more likely to succesfully finish, but were more wobbly and thus had less smooth surfaces.

Surface Finish

As mentioned previously, most prints were quite wobbly, resulting in surfaces that are not very smooth. Due to the addition of glycerin, the material itself has a smooth texture, but surfaces as a whole are not smooth, due to the variation in layer protrusion. This can be slightly improved by decreasing the layer height, but still a substantial amount of variation in layer protrusion will be created.

Reflow rPLA (1kg)
€26.62

Reflow rPETG (1kg)
€33.88

Material Mix (1kg)
€23.60

Figure 54: Price comparison between material mix and reference materials

Price

The price of the material mix is a total of the costs of the individual components, the processing that is need for them and the process of making the mixture.

Eggshells

As discussed in Chapter 5 (Eggshell), it is estimated to cost breaker plants $100.000 annually to have the eggshells processed and brought to landfills (Sonenklar, 1999). The demand for eggshells does not match their availability, so most of them are considered waste. By purposing the eggshells and making them a valuable resource rather than a waste product, the eggshells could actually form an additional source of income for the breaker plants. Currently, eggshell powder is commercially available as a calcium supplement for dogs, costing around €9.95 per 300 grams which equates to €33,17 per kilo (Agradi, 2022). Wholesale prices are likely to be a lot lower and could be further lowered if demand for eggshell increases as processing costs will be distributable over larger amounts of material. Alternatively, if consumers are to make their own material mix,they could collect their own eggshells, which would be free.

Sodium Silicate/Waterglass

Waterglass was bought at a price of €6.20 per 500 mL(Gerstaecker, 2022), or €12.40 per liter. No density was provided by the manufacturer. According to the U.S. Coast Guard, sodium silicat has a density of between 1.1 and 1.7 g/cm^3 at 20 ° C (U.S. Coast Guard, 1999), whereas The Conservation and Art Materials Encyclopedia Online (CAMEO) reports a density of between 1.3 and 1.5 g/cm^3 for waterglass in liquid state. For calculations a value of 1.35 g/cm^3 is used, falling in the range of both sources. Assuming this density is correct, waterglass costs €9.19 per kilo. Wholesale prices are not available, but are likely to be considerably cheaper.

Glycerine

Glycerine is available as a moisturizer for skin. The glycerine used in this project was bought at Holland & Barret for €2.75 per 150mL (Holland & Barrett, 2022). Density of the glycerine was not profided by the manufacturer, nor tested, but in other research a density of 1.261g/cm^3 (Rochester Institute of Technology, n.d.) was found. This equates to a price of €2.75 per 189.15 gram, or €14.54 per kg. Wholesale prices are not available, but are likely to be considerably cheaper.

Total

Based on the found prices for the components, the price per kilogram of the material mix can be calculated, taking into account at what ratios they were used.

Eggshell wt % = 26 / (26 + 16 + 2) * 100% = 59.09%
Eggshell price per kg of material mix = 59.09% of €33,17
= €19.60

Waterglass wt % = 16 / (26 + 16 + 2) * 100% = 36.36%
Waterglass price per kg of material mix = 36.36% of
€9.19 = €3.34

Glycerine wt % = 2 / (26 + 16 + 2) * 100% = 4.55%

Glycerine price per kg of material mix = 4.55% of €14.54 = €0.66

Total price per kg of material mix = €19.60 + €33.34 + €0.66 = €23.60

Pricing for the reference materials is set at €26.62 for a 1kg roll of rPLA (Reflow, 2022a) and €33.88 for a 1kg roll of rPETG (Reflow, 2022b), making the material mix the cheapest option at €23.60 per kg.

However, when taking density of the materials in consideration, things shift a bit. From measurements it was found that the material mix is roughly 27.9% more dense than rPLA and 25.6% more dense than rPETG. This means that with 1kg of material mix, less volume, and thus less models can be printed than with rPLA and rPETG. When pricing is compared based on volume, the price of the material mix should be increased with 27.9% to compare it well with rPLA and increased by 25.6% to compare it well with rPETG.

Price material mix at same volume as 1kg of rPLA = €23.60 * 1.279 = €30.18

Price material mix at same volume as 1kg of rPLA = €23.60 * 1.256 = €29.64

This suggests that pricing for the material mix falls in between the prices for rPLA and rPETG. However, this is at commercial prices for all components, rather than wholesale. Final pricing for the material mix should be considerably cheaper. As mentioned in Chapter 5, disposal of eggshells currently costs breaker plants $100.000 annually. Applications of eggshells are limited, driving up the price of processed eggshells. If more applications for eggshells are found, scaling up their processing should decrease prices, while turning the eggshells into revenue for the breaker plants.

Furhtermore it should be noted that the calculations for density are not very accurate and volumetric price calculation should be considered an approximate estimation. In calculating the volume of the specimens, their shape was simplified to a beam with uniform measurements and sharp corners, while in reality shapes were not perfect beams and vertical edges had been rounded off with a 1mm radius. On top of that, the weight of specimens was measured at a precision of 0.1 gram, which is relatively unaccurate considering specimens weighed rougly 2.7 gram. The found values for density of rPLA and rPETG deviated from the values given by Reflow (Reflow, 2021a; Reflow, 2021b) by around 7%, see Appendix D, but deviations were fairly consistent, especially for rPETG, so it was deemed accurate enough to do a rough comparison between the materials and make an approximate estimation of volume-based pricing for the material mix.

Environmental Impact

The environmental impact of printing with the material mix is dependent on a few factors, being the energy use of the printing process, the impact of the individual components in the material mix and the impact of fabricating the material mix.

Printing Process

The material mix that was developed in this project could succesfully be printed at room temperature and no heating of nozzle, nor printbed was needed. As it was found that the hot end and heatbed are responsible for 72.9% of the energy consumption of the FDM printing process (Nguyen, 2021), it would suggest a considerable reduction of energy use as a result of operating the printer should have been made. However, although the printer's heating components were disabled while printing with the made material mixes and thus didn't use any energy, the modified printhead was found to be considerably more heavy than than the original printhead, as the original printhead weighs 578.5 gram, while the modified printhead weighs 751.5 gram. On top of that, the modified printhead requires the 'filament' to be loaded on the printhead, whereas in conventional FDM printing, the roll of filament is usually mounted somewhere on the frame, where is sits stationary. The higher weight of the modified printhead and the added weight of the material mix require the stepper motors on the X and Z to move around more mass, resulting in a higher energy consumption. On top of that, the material mix has a higher density than the plastic filaments so also the stepper motor on the Y-axis has to move around more mass, resulting in a higher energy consumption.

Overall, taking away the need to heat up material nor printbed should make a more substantial reduction in energy consumption of FDM printing than energy consumption is increased due to the added weight of the modified printhead and material. Energy consumption was not measured however, so it can only be assumed that there is a overall reduction in energy consumption.

Material Mix Components

Impact of the material mix itself is based on the background and impact of all individual components.

Eggshell powder is a completely natural material that is fully biodegradable. It can be used as a fertilizer for soil, as calcium carbonate is a crucial mineral for strenghtening plants' cell walls and other minerals inside eggshells, including potassium, phosphorus and magnesium, also help plants grow. In other words, eggshells have the potential to benefit the environment rather than being detrimental.

Sodium silicate, or waterglass, can be acutely toxi due to its high pH value. It has been found that it can be moderately toxic to aquatic organisms and slightly toxic to terrestrial organisms (Occidental Chemical Corporation, 2013). However, once diluted, it will become silica Occidental Chemical Corporation, 2013), a commonly naturally occuring element that can be found in sand and quartz (Matta, 2017), which is completely harmless. Silica also does not bioconcentrate up the food chain (Occidental Chemical Corporation, 2013). As a sidenote, in the past waterglass was also used for the preservation of eggs, as it was found that eggs would last up to five months when stored in a mixture of one part waterglass to nine parts of boiled water (Hall, 1945).

Glycerin/glycerol is an alcohol that occurs naturally and can be found in the human body. Most glycerin is a byproduct of biodiesel production (Goodman, 2008) However, when released to water, it depletes the oxygen content of the water, which potentially causing fish and other organisms to suffocate. Releasing large amounts of glycerin to bodies of water should thus be avoided.

Bending Test

Although the testing of mechanical properties was considered out of scope for the most part, a bending test was performed to have some idea how well the developed material mix compares to the recycled filaments that were used for reference.

For the bending test, ASTM standard D 790-03 was followed as much as possible. Unfortunately it was found that the test specimens, that were made for the test, did not meet all equirements set by the standard. Dimensions for the test specimens were taken from a sample specimen that was found at the bending machine. After printing all specimens, it was found that these dimensions do not meet the criteria set by the ASTM standard. According the standard, the specimen depth to specimen length ratio should be 1 : 16 or smaller (Raheem, 2019). The found sample however, had a depth of 4.00mm and a length of 58.40mm, leading to a ratio of 1 : 14.6. Due to the limited time that was available for performing the test, it was chosen to perform with the samples that had already been printed, despite the fact that they did not meet the criteria set by the standard.

Test Preparation

In preparation for the test, a few variables have to be set:

The **overhang** at each side has to be at least 10% of the support span, but no smaller than than 6.4mm. Considering 10% of the entire specimen length is, with a value of 5.84mm, already smaller than the minimum value of 6.4mm, the overhang will be set at 6.4mm rather than taking 10% of the span width.

The **span width** can now be calculated based on the length that remains after subtracting the overhang at each side of the specimen. Due to the diversity in dimensional accuracy of the materials, span width was determined for each material group seperately. For each material, the length of the shortest specimen was used to calculate the span width, see Table 5. Tests were performed per material group and span width was adjusted before starting tests with a different material group.

Material	Shortest sample (mm)	Overhang (mm)	Span width (mm)
rPLA	*58.10*	*6.4*	*45.30 mm*
rPETG	*58.22*	*6.4*	*45.42*
Material Mix	*57.14*	*6.4*	*44.34*

Table 5: Span Width of the three material groups

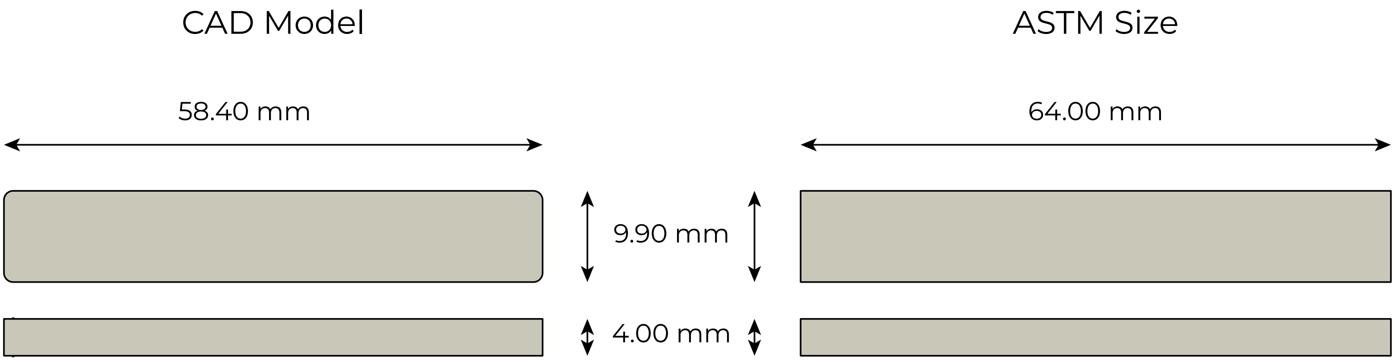
The next step is to determine the **rate of crosshead motion**, or the speed at which the loading nose is pressed down at the specimen. This speed can be calculated using a formula:

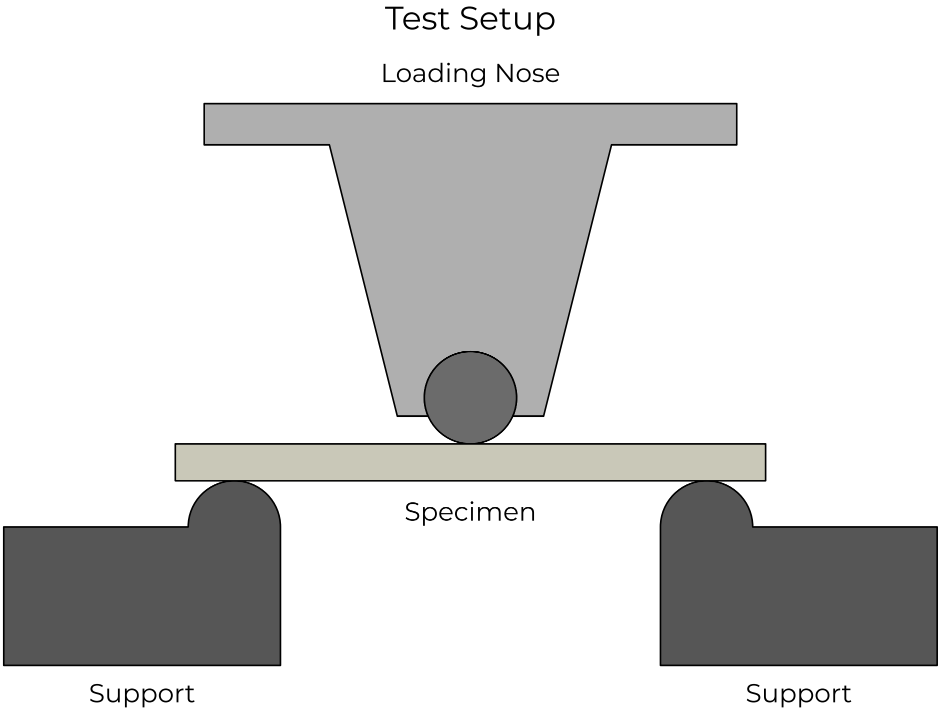
$$R = ZL^2/6d$$

where:
R = rate of crosshead motion, in mm/min
L = support span, in mm
d = depth of specimen, in mm
Z = rate of straining of the outer fiber, in mm/mm/min. Z shall be equal to 0.01.

Calculating the rate of crosshead motion for each of the materials results in the following values:

$$R_{rPLA} = 0.844... = 0.84 \text{ mm/min}$$
$$R_{rPETG} = 0.861... = 0.86 \text{ mm/min}$$





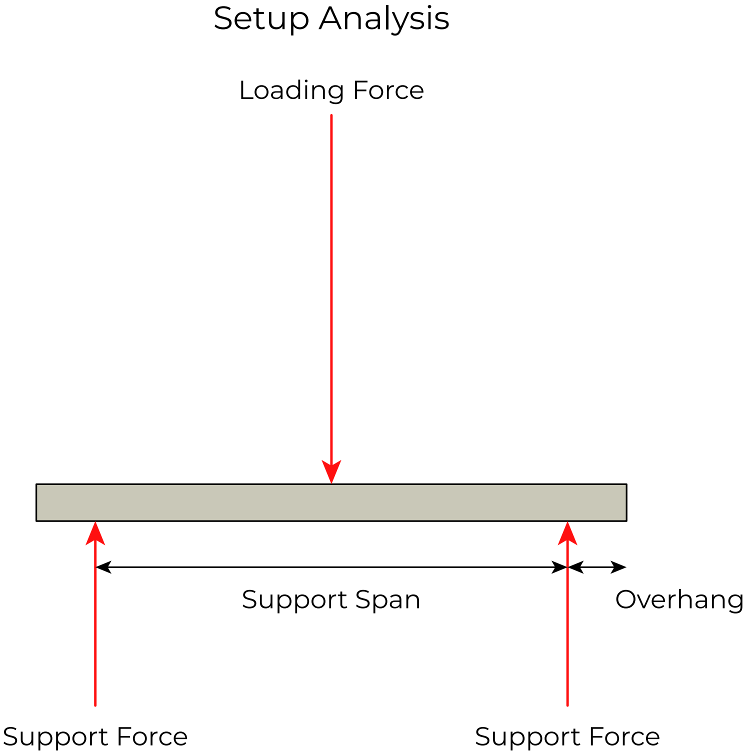


Figure 55: Simplified sketch of bending test working principle

Figure 56: Zwick/Roell Z010

$$R_{MaterialMix} = 0.869... = 0.87 \text{ mm/min}$$

Unfortunately, here yet another mistake was made as it was assumed that the values for R were in mm/s rather than mm/min so they were multiplied by 60, rather than taken as they were. This means that the speed was a factor of 60 too high. The used values were:

$$R_{rPLA} = 0.844... * 60 = 50.67 \text{ mm/min}$$
$$R_{rPETG} = 0.861... * 60 = 51.70 \text{ mm/min}$$
$$R_{MaterialMix} = 0.869... * 60 = 52.15 \text{ mm/min}$$

The final step would be to calculate the **midspan deflection**, which is where the specimen has reached the maximum strain of 0.05mm/mm in its outer surface. The test should be stopped when this value is reached or when the sample breaks before this reached is reached. The formula for midspan deflection is as follows:

$$D = rL^2/6d$$

where:
D = midspan deflection, in mm
r = strain, in mm/mm, which is set at 0.05 mm/mm
L = support span, in mm
d = depth of specimen, in mm

Calculating the midspan deflection for each material group results in:

$$D_{rPLA} = 4.222... = 4.22 \text{ mm}$$
$$D_{rPETG} = 4.308... = 4.31 \text{ mm}$$
$$D_{MaterialMix} = 4.345... = 4.35 \text{ mm}$$

Midspan deflection was not used in the test however. It was considered more interesting to see the maximum deflection and force each material could take rather than limiting it to the maximum midspan deflection.

Test Procedure

Now that all testing parameters have been determined, the actual test can be carried out. Testing was done on a Zwick/Roell Z010, see figure 56.

Spanwidth was set manually by rotating the screw on the support block until the appropriate value had been reached and the values span width, specimen thickness and rate of crosshead motion were set in the control software.

After adjusting the support span and setting the parameters in the control software, specimens were loaded onto the machine one by one and tested. Settings were adjusted when switching material.

Test Results

Regardless of the mistakes that were made in terms of specimen length and rate of crosshead motion, the results were found to be very reproducable and thus allow a decent comparison of part of the mechanical behaviour of the three different materials. Table 6 shows result for the average max force, average deflection at max force, average force at break and average deflection at break for material groups, while Appendix E shows the results for each individual specimen.

The results show that the found material mix is signifantly weaker than the reference materials. Whereas rPLA and rPETG can handle forces up to 245.84N and 198.59N respectively, the found material mix can only handle 8.53N, less than 5% of the (plastic) filaments.

If the maximum midspan deflection had been used during the tests, the rPLA and rPETG specimens may not even have fully broken. When analysing the graphs in figure 57 and the results in table 6, it can be seen that the maximum midspan deflection is reached around the same time as the max force is reached and the specimen is already deforming plastically. Had maximum midspan deflection been applied, (some of) the rPLA specimens would likely not have fully broken, but just have been deformed. The results do show that rPLA is fairly brittle as the specimens can bend relatively little after the max force has been reached. This means that the specimens can only take minor plastic deformation before breaking. Analysing the rPETG graphs is more difficult as two tops can be seen. The first top is likely to be the actual top, where the material starts to deform plastically, whereas the second top is caused by the specimens sliding down the supports as a result of the downward motion of the nose. Had maximum midspan deflection been used, the test would have stopped earlier and there would not have been two tops. Based on this assumption, the maximum midspan deflection seems to fall under the elastic deformation part of the graphs, meaning that the rPETG specimens would not have broken or plastically deformed if the maximum midspan deflection had been used. Furthermore, rPETG seems the most ductile material out of the three as it can handle more

	rPLA	rPETG	Material Mix
Specimens tested	*10*	*6*	*7*
Average Max Force (N)	*245.84*	*198.59*	*8.53*
Average Deflection at Max Force (mm)	*4.23*	*11.66*	*0.79*
(Average) Force at break (N)	*120.45*	*99.19*	*7.77*
Deflection at break (mm)	*5.03*	*14.64*	*0.86*

Figure 6: Graphs of all bending tests

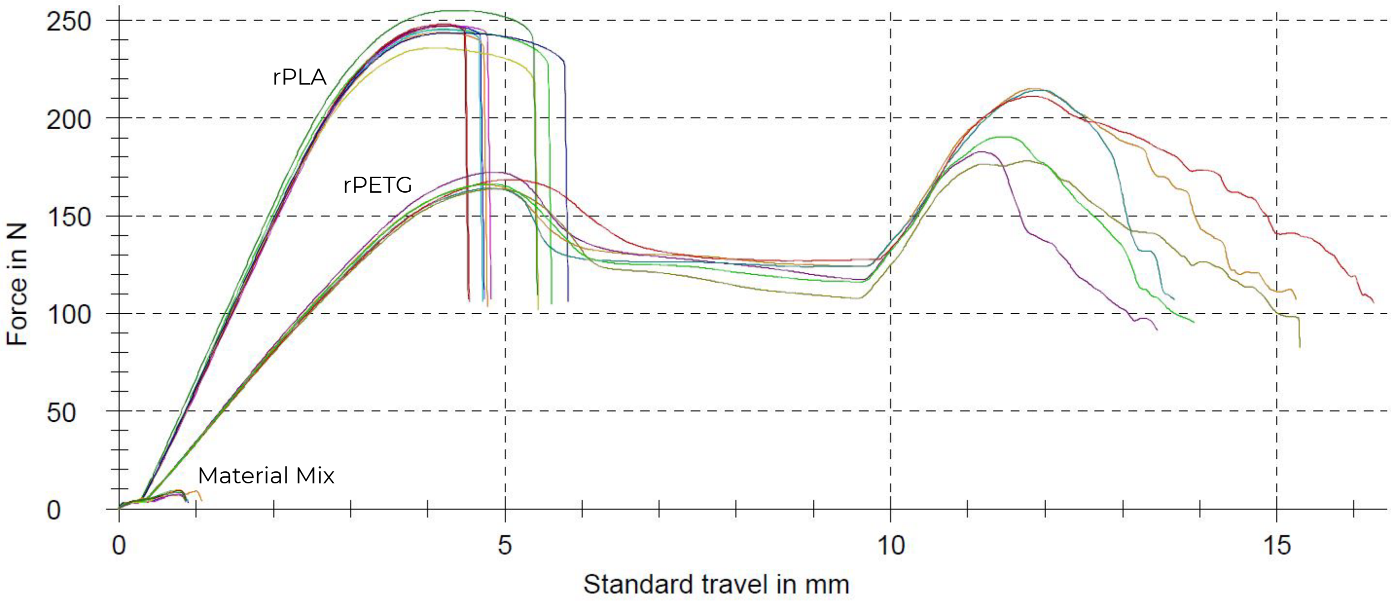


Figure 57: Graphs of all bending tests

plastic deformation before breaking than the other materials. Specimens made with the material mix did not come close to the maximum midspan deflection so their results are unaffected by it. The max force of only 8.53N show that the material mix is extremely weak and the small difference between deflection at max force and deflection at break show that the material mix is extremely brittle. A plastic deformation of only 0.07mm was enough to break the specimens.

Upon closer examination of the crosssection of the material mix specimens, it was found that there is a considerable amount of porosity, which is likely part of the reason why the material mix performed so poorly in the bending test, see figure 58-60. Airpockets form weaknesses in the material and prints are more likely to break at places where those airpockets are located. If the airpockets were to be prevented, the specimens would likely perform better in any mechanical tests, although it should not be expected that performance would match the performance of rPLA and rPETG specimens.

Apart from the porosity it is interesting to see that the crosssections match well with the test results. The rPLA specimen has a very flat and clean break, matching with the brittleness that was found in the test data. The rPETG specimen shows a lot more deformation due to its more ductile behaviour which makes it handle a lot more plastic deformation before breaking. The Material Mix specimen has a somewhat flat surface, matching with the brittleness that was found in test results, but it’s not completely flat and larger airpockets are being revealed, that seem to attract the break, proving that they cause the material mix to be weaker.

WATCH ME BEING BENT!

Figure 58: Crosssection break rPLA specimen 2

WATCH ME BEING BENT!

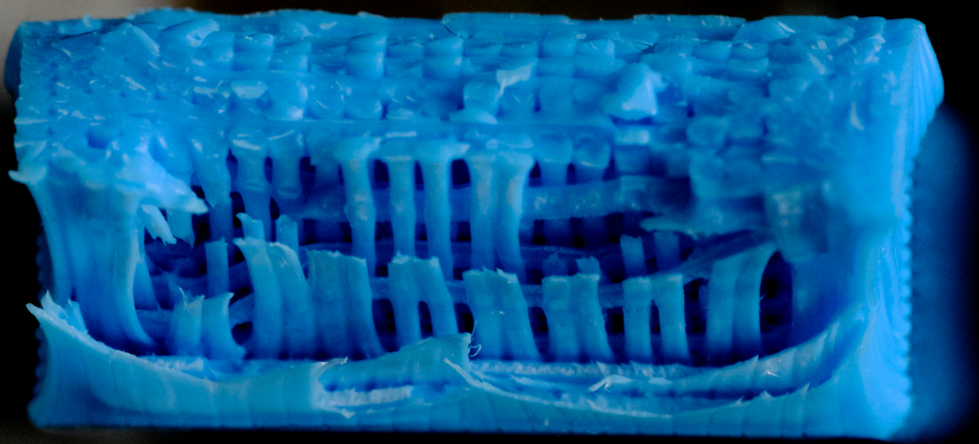


Figure 59: Crosssection break rPETG specimen 4

WATCH ME BEING BENT!

Figure 60: Crosssection break Material Mix specimen 1

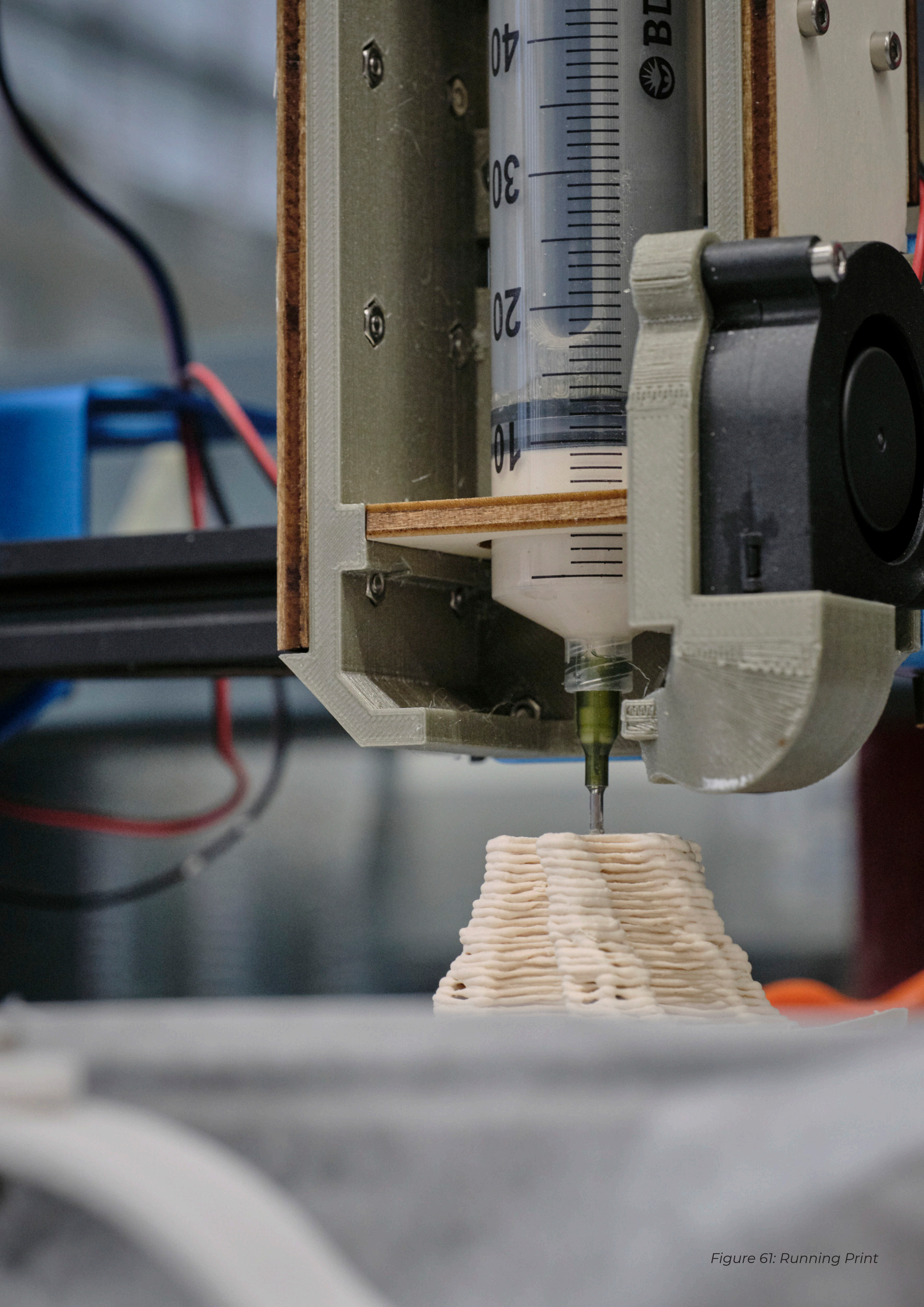


Figure 61: Running Print

Ch. 9 | Conclusion & Recommendations

Now that the material mix has been assessed on the defined criteria, as well as having gained some insight into the mechanical performance it is possible to conclude how well the material mix meets the goal of the project. On top of that, recommendations for future research will be discussed, that could be done in an attempt to further improve printing results

Conclusion

Unfortunately, the found material mix performs mediocre at best. In all tests that have been done throughout the project, material mixes, printer modification, printing procedure and slicing settings have been improved in an iterative manner, but the quality of prints made with the found material mix still don't even come close to the quality of prints made with the plastic filaments. Prints made with the material mix cannot match prints made with plastic filaments in most of the chosen criteria. The only criteria where the material mix performs decently well are pricing and the environmental impact. The practice of printing with paste does show potential as the print results clearly resemble the CAD model to a decent extend and there seems to be a clear environmental benefit of printing with the material mixes. However, the wobbliness of the prints, vulnerability due to brittless and the more complex printing procedure show that still a lot of development has to be done in order to make both material mixes and printing procedure be an acceptable alternative for conventional FDM printing, irregardless of its environmental benefit. Current printing results make it suitable for models that are for aesthetic purposes, but not for functional models and prototypes where mechanical properties and dimensional accuracy are of importance. Based on those results, it has to be concluded that goal 1, to develop a material mix that is suitable for FDM, is less detrimental for the environment than the plastic filaments and could serve as a replacement for them, unfortunately has not been met.

Goal 2, to modify a conventional FDM printer in order to print with paste-like material mixes, was succesfully reached. The printer works generally well and any failures in prints are likely caused by the material mix and not the printer itself. Behaviour of the printer was found to be consistent and the modification was quite easy to use. What makes working with paste-like materials difficult and cumbersome is that it is difficult to add the material mix to the syringe well and the material tends to dry inside the nozzle, clogging it up. Sticking a needle or nail into the nozzle would often solve the clogging issue, but in some cases the complete syringe had to be removed, which takes a lot of time and it created the risk that calibration of the printer would be off due to variations in the extend to which the nozzle was screwed into the syringe. On several occasions, the nozzle would not screw in as much as small amounts of material had nestled in the screw thread in the syringe, preventing the nozzle to be screwed in more. As a result of that, the nozzle would jam into the printbed, tearing up the baking paper or scratching the polyethylene sheet.

The third goal, to develop an appropriate procedure for testing and printing with paste-like material mixes has also been succesfully met. A full roadmap has been set up in which the order of steps to have the highest chance of succesful prints has been set up and the most important slicing settings have been identified. Using the roadmap, most printing issues that could lead to print failure, can be prevented and print issues as a result of ‘wrong‘ slicer settings can be identified and solved.

All in all, the project can be considered a success as interesting results have been achieved, even though they are not as great as was hoped. Their is a clear potential for printing with paste-like materials and future development bring print quality closer to that of the plastic filaments.

Recommendations

In this final section, recommendations for future researches will be discussed. Based on what was learned throughout the research, potential topics for future research have been found. Doing this research might help improve printing results, bringing printing with pastes more on par with conventional FDM printing.

Lowering eggshell brittleness

All eggshell recipes ended up being very brittle especially when compared to prints made with the plastic filament. In an attempt to reduce the brittleness of the eggshell powder, tests have been done in which vinegar, glycerol and glycerine were added to eggshell powder. Although some changes in properties were witnessed, the brittleness remained an issue. Based on these results, it seems like the brittleness is an inherent property of eggshells, but perhaps, in future research, an additive or binder can be found that solves the brittleness issue of the eggshell, which could potentially improve the usability of the usability of the material mix.

Measuring energy consumption

Energy consumption of the modified printer was estimated to be lower as a result of removing the need to heat up the printhead and print bed. This is only an assumption however and in the future measurements should be done in energy consumption of the printer to back this claim up.

Functionalization materials

Functionalization of the material mix was considered to test, but has not been done in the end. In further research it could be tested whether there are functionalization materials that could improve the texture or other properties of the material mix and prints.

Eliminating porosity

Prints showed considerable amounts of porosity at crosssections of breaks, even though no airbubbles were visible in the material mix after mixing. This porosity is likely part of the reason why the prints are so brittle and why performance was so poor in the bending test in comparison with the reference materials. In future research it would be interesting to see whether this porosity can be eliminated and what effect that would have on mechanical properties of the material mix. Two ways that porosity could potentially be lowered is by better mixing or by putting the material in a vacuum oven prior to printing with it. Testing whether a vacuum oven could lower porosity of the prints was considered, but unfortunately didn't fit the timeframe of the project.

Viscosity definition

In material mix development, ratios of components were alternated in an interative fashion, until a ratio was found that worked best. Viscosity was used as a indication whether the developed material mix would likely perform well or not, but viscosity was eyeballed, rather than measured. In future tests it is recommended to find out what viscosity gives the best printing results. In hindsight, the developed material mixes may not have been viscous enough, which might be part of the reason why the print surfaces were so wobbly. A more viscous material mix would likely retain shape better and provide more support for layers placed on top of it.

Calibration Conistency

The Luer Lock needles that were used as nozzles on the printer had to be screwed into the syringe. This screwing action created a margin for error as the nozzle would not always be screwed in as much, especially when some material had nested itself inside the screw thread. As a result of this, the distance between the nozzle and the printbed was not always consistent. In future research as solution for this issue should be found, in order to make sure printing performance is as consistent as possible.

Figure 61: Initial Design for plunger

Ch. 10 | Personal Reflection

The project has been an interesting journey for me. There was a definite match between the project and my personal interests in 3D printing and sustainability, which were the foundation of this project, as well as my love for working hands-on, which I got to do plenty of in the form of building and installing modifications for the printer and doing the test prints themselves.

Looking back at the project, I feel torn about the way the project has unfolded. On the one hand I'm happy by what I managed to do: I've succesfully modified the printer to enable it to print with paste, with no prior experience in doing something like that and with little experience in coding. And I managed to develop a material mix recipe that can be printed and gives decent results. On the other hand, it's been very challenging and the project has taken me a lot longer than was originally planned. Everything I've done in the project ended up more challenging than expected and there have been a lot of unforseen obstacles. It was only since the fourth version of the printer modification that I felt like the printer was doing what it was supposed to and the test results started to get interesting at a point in time where I really had to stop testing and start wrapping things up. As a result of that I can't help but feel like I'm having to finish this project with mediocre print results, even though I knew from the beginning that not finishing with an amazing material mix recipe was a likely option.

I've never done any project like this, neither in size nor subject. And that's exactly what made doing it so challenging but also so fun. Although the end-result is not what I wanted to have, it is interesting to see how much I've learned about working with materials and trying to print with them. I now have an understanding of the challenges of working and printing with these paste-like material mixes that I didn't have before. And I'm sure I'll be able to have a better, more structured approach for future projects from what I've learned through the challenges that I met in this project.

The support that I have gotten from my supervisory team, dr. Ghodrat and dr. Faludi, has been essential for the progress that I've made througout this project. Their knowledge and help has given the project new directions several times, which also resulted in breakthroughs several times. My only regret is not having talked to them more regularly as that may have made the outcome of this project even more interesting. I don't think I've been the easiest student they have dealt with and I'm thankful that they've supported me throughout all the ups and downs of the project.

To conclude, I'm thankful to have had the opportunity to do this project and hope that my journey in developing, working and FDM printing with paste-like materials will help to make the journeys of others in this even the tiniest bit easier. Making FDM printing more environmentally sustainable is a goal that should still be pursued and I'm curious to see what progress others can make for it.

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Personal Communication

Constantijn Crijnen, YouTuber and 3D printing expert

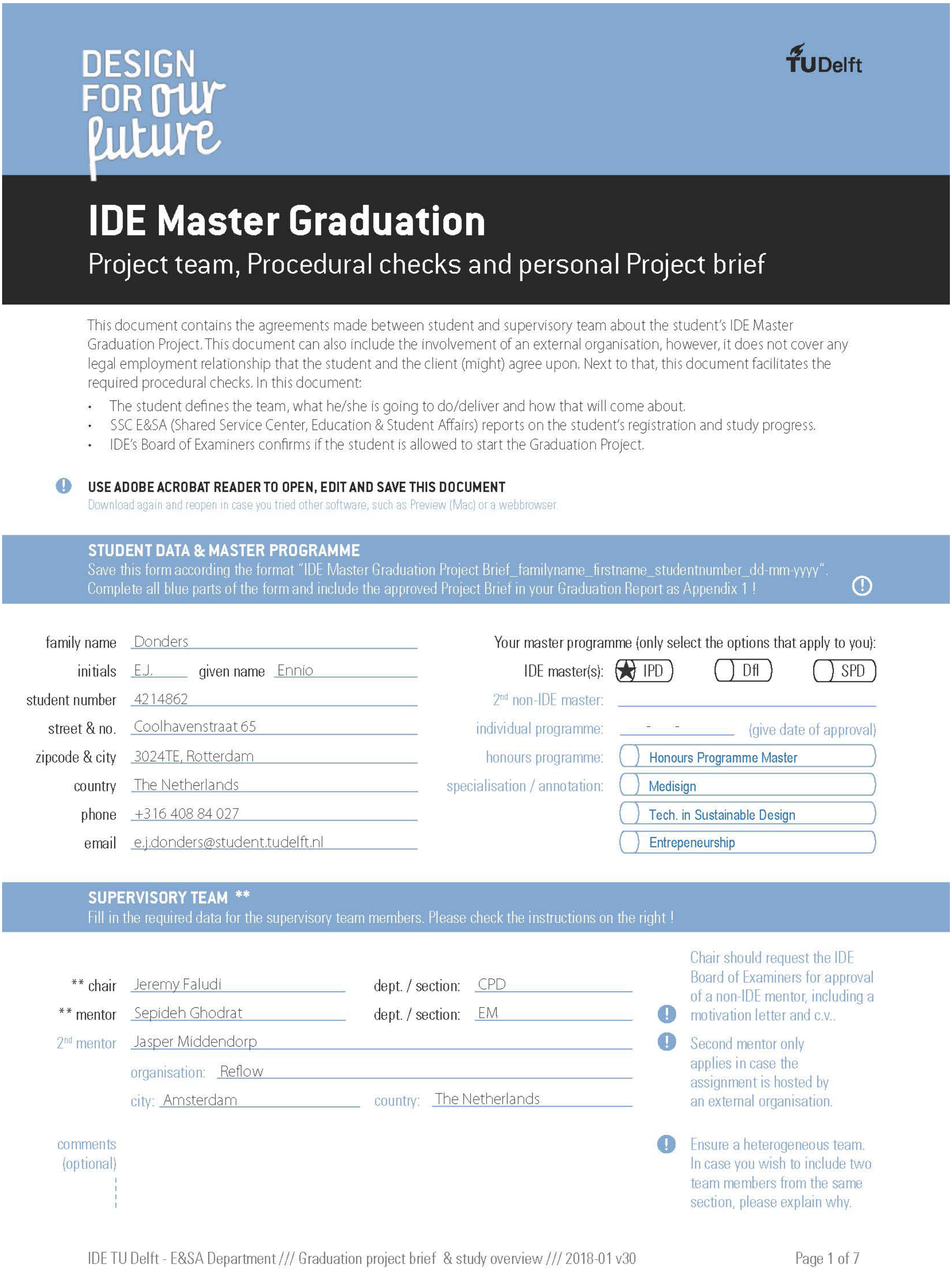
Yao van den Heerik, 3D printer developer and owner of VormVrij

Prof. dr. ir. Kaspar Jansen, Professor of Emerging Material the TU Delft

Dr. ir. Marita Sauerwein, 3D printing expert

Appendices

Appendix A - Project Brief



DESIGN FOR our future

TU Delft

IDE Master Graduation

Project team, Procedural checks and personal Project brief

This document contains the agreements made between student and supervisory team about the student's IDE Master Graduation Project. This document can also include the involvement of an external organisation, however, it does not cover any legal employment relationship that the student and the client (might) agree upon. Next to that, this document facilitates the required procedural checks. In this document:

- The student defines the team, what he/she is going to do/deliver and how that will come about.
- SSC E&SA (Shared Service Center, Education & Student Affairs) reports on the student's registration and study progress.
- IDE's Board of Examiners confirms if the student is allowed to start the Graduation Project.

USE ADOBE ACROBAT READER TO OPEN, EDIT AND SAVE THIS DOCUMENT
Download again and reopen in case you tried other software, such as Preview (Mac) or a webbrowser.

STUDENT DATA & MASTER PROGRAMME

Save this form according the format "IDE Master Graduation Project Brief_familyname_firstname_studentnumber_dd-mm-yyyy". Complete all blue parts of the form and include the approved Project Brief in your Graduation Report as Appendix 1 !

family name: Donders
initials: E.J. given name: Ennio
student number: 4214862
street & no.: Coolhavenstraat 65
zipcode & city: 3024TE, Rotterdam
country: The Netherlands
phone: +316 408 84 027
email: e.j.donders@student.tudelft.nl

Your master programme (only select the options that apply to you):
IDE master(s): ● IPD ○ DfI ○ SPD
2nd non-IDE master:
individual programme: - - (give date of approval)
honours programme: ○ Honours Programme Master
specialisation / annotation: ○ Medisign
○ Tech. in Sustainable Design
○ Entrepeneurship

SUPERVISORY TEAM **

Fill in the required data for the supervisory team members. Please check the instructions on the right !

** chair: Jeremy Faludi dept. / section: CPD
** mentor: Sepideh Ghodrat dept. / section: EM
2nd mentor: Jasper Middendorp
organisation: Reflow
city: Amsterdam country: The Netherlands
comments (optional):

Chair should request the IDE Board of Examiners for approval of a non-IDE mentor, including a motivation letter and c.v..

Second mentor only applies in case the assignment is hosted by an external organisation.

Ensure a heterogeneous team. In case you wish to include two team members from the same section, please explain why.

IDE TU Delft - E&SA Department /// Graduation project brief & study overview /// 2018-01 v30 Page 1 of 7

Procedural Checks - IDE Master Graduation

APPROVAL PROJECT BRIEF

To be filled in by the chair of the supervisory team.

chair Jeremy Faludi date - - signature

CHECK STUDY PROGRESS

To be filled in by the SSC E&SA (Shared Service Center, Education & Student Affairs), after approval of the project brief by the Chair.
The study progress will be checked for a 2nd time just before the green light meeting.

Master electives no. of EC accumulated in total: ______ EC

Of which, taking the conditional requirements into account, can be part of the exam programme ______ EC

List of electives obtained before the third semester without approval of the BoE ______

○ YES all 1st year master courses passed

○ NO missing 1st year master courses are:

name ______ date - - signature ______

FORMAL APPROVAL GRADUATION PROJECT

To be filled in by the Board of Examiners of IDE TU Delft. Please check the supervisory team and study the parts of the brief marked **.
Next, please assess, (dis)approve and sign this Project Brief, by using the criteria below.

- Does the project fit within the (MSc)-programme of the student (taking into account, if described, the activities done next to the obligatory MSc specific courses)?
- Is the level of the project challenging enough for a MSc IDE graduating student?
- Is the project expected to be doable within 100 working days/20 weeks ?
- Does the composition of the supervisory team comply with the regulations and fit the assignment ?

Content: ○ APPROVED ○ NOT APPROVED

Procedure: ○ APPROVED ○ NOT APPROVED

comments

name ______ date - - signature ______

Initials & Name E.J. Donders Student number 4214862

Title of Project Using materials derived from waste streams for 3D Printing

Using materials derived from waste streams for 3D Printing project title

Please state the title of your graduation project (above) and the start date and end date (below). Keep the title compact and simple. Do not use abbreviations. The remainder of this document allows you to define and clarify your graduation project.

start date 30 - 06 - 2021

30 - 11 - 2021 end date

INTRODUCTION **

Please describe, the context of your project, and address the main stakeholders (interests) within this context in a concise yet complete manner. Who are involved, what do they value and how do they currently operate within the given context? What are the main opportunities and limitations you are currently aware of (cultural- and social norms, resources (time, money,...), technology, ...).

Fused Deposition Modeling (FDM) and Fused Filament Fabrication (FFF), have gained a lot of popularity over the last few years with dozens of companies developing printers and already hundreds of options available to buy. 3D printing has become more affordable than ever with printers being available for as little as 150 euros. These printers have become a go-to for designers, architects, artists and hobbyists, allowing them to make quick prototypes, display models, artwork and replacement parts for household items. Whereas making a part or prototype with traditional techniques can take several days, weeks or even months, making one with FDM/FFF can be done in just a few hours.

The most commonly used materials for FDM/FFF are the plastics PLA, ABS and PETG, each having their own set of advantages and disadvantages and each requiring different settings to print with. One of the downsides of these materials is the need of both valuable and non-renewable resources for their production. ABS and PETG are fossil-based plastics and the production of PLA relies on the use of fossil-fuels as a source of energy. PLA is made by the fermentation of renewable resources such as corn, sugar, potato, and cassava, which are also used as food for people and animals.

There is a need for printable materials that offer the same freedom in design as the commonly used filaments (PLA, ABS and PETG) offer, but are less reliant on non-renewable and valuable resources.

In order to be a suitable alternative to the commonly used filaments, the material mix that will be created must perform similarly well or better than the commonly used filaments. That is why the material mixes that are created throughout the project will be assessed based on the following criteria:

1. Print-ability (ability to extrude & self-support, including stopping & starting cleanly, printing time)
2. Dimensional accuracy (not shrinking or warping, matching CAD model dimensions)
3. Resolution (primarily layer height in z direction)
4. Surface finish (smooth and uniform surfaces, not rough or broken)
5. Price (material cost per kg)
6. Environmental Impact (carbon footprint, water expenditure, reliance on non-renewable sources)

To put these values into perspective, rPLA and rPETG (as produced by the Reflow, the client for this project) will be used as reference materials. The 'r' in their names indicate that these filaments are 100% recycled.

The environmental impact aspect of the materials will be based on literature. If time allows, a LCA will be used to get a more precise indication of the environmental impacts of the various materials and thus whether the newly developed material mix has a lower environmental impact than the reference materials (rPLA and rPETG).

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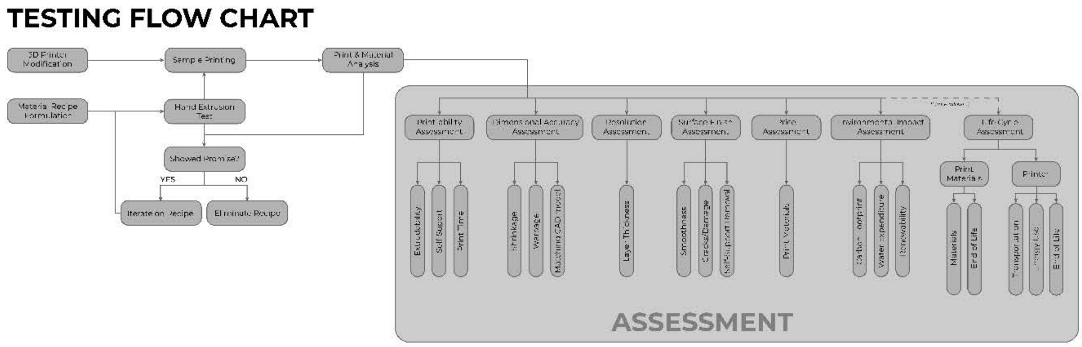
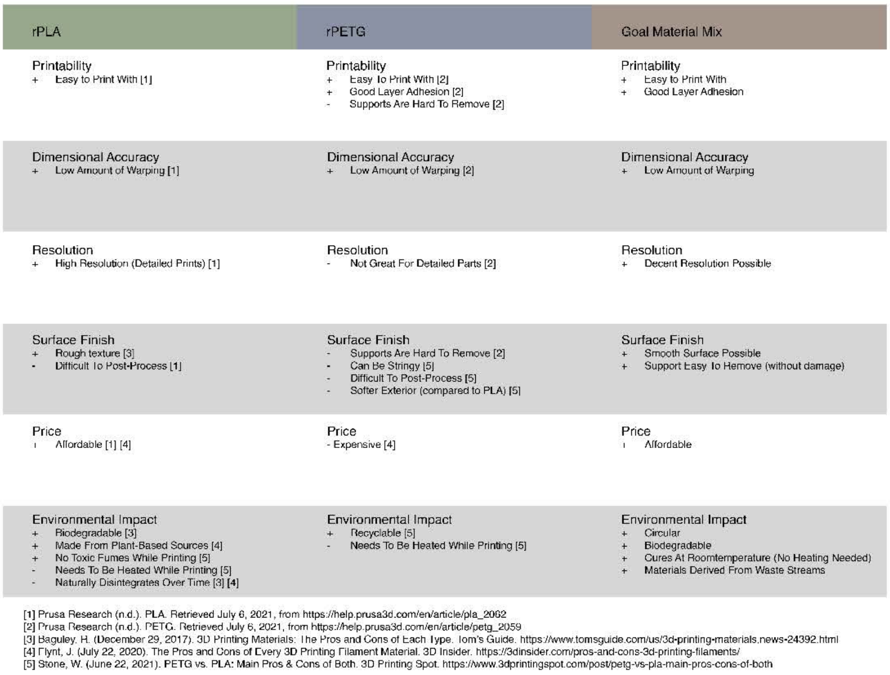


image / figure 1: Table of properties to measure success



rPLA	rPETG	Goal Material Mix
Printability + Easy to Print With [1]	Printability + Easy To Print With [2] + Good Layer Adhesion [2] - Supports Are Hard To Remove [2]	Printability + Easy to Print With + Good Layer Adhesion
Dimensional Accuracy + Low Amount of Warping [1]	Dimensional Accuracy + Low Amount of Warping [2]	Dimensional Accuracy + Low Amount of Warping
Resolution + High Resolution (Detailed Prints) [1]	Resolution - Not Great For Detailed Parts [2]	Resolution + Decent Resolution Possible
Surface Finish + Rough texture [3] - Difficult To Post-Process [1]	Surface Finish - Supports Are Hard To Remove [2] - Can Be Stringy [5] - Difficult To Post-Process [5] - Softer Exterior (compared to PLA) [5]	Surface Finish + Smooth Surface Possible + Support Easy To Remove (without damage)
Price + Affordable [1] [4]	Price - Expensive [4]	Price + Affordable
Environmental Impact + Biodegradable [3] + Made From Plant-Based Sources [4] + No Toxic Fumes While Printing [5] - Needs To Be Heated While Printing [5] - Naturally Disintegrates Over Time [3] **[4]**	Environmental Impact + Recyclable [5] - Needs To Be Heated While Printing [5]	Environmental Impact + Circular + Biodegradable + Cures At Roomtemperature (No Heating Needed) + Materials Derived From Waste Streams

[1] Prusa Research (n.d.). PLA. Retrieved July 6, 2021, from https://help.prusa3d.com/en/article/pla_2062
[2] Prusa Research (n.d.). PETG. Retrieved July 6, 2021, from https://help.prusa3d.com/en/article/petg_2059
[3] Baguley, H. (December 29, 2017). 3D Printing Materials: The Pros and Cons of Each Type. Tom's Guide. https://www.tomsguide.com/us/3d-printing-materials,news-24392.html
[4] Flynt, J. (July 22, 2020). The Pros and Cons of Every 3D Printing Filament Material. 3D Insider. https://3dinsider.com/pros-and-cons-3d-printing-filaments/
[5] Stone, W. (June 22, 2021). PETG vs. PLA: Main Pros & Cons of Both. 3D Printing Spot. https://www.3dprintingspot.com/post/petg-vs-pla-main-pros-cons-of-both

image / figure 2: Comparison between goal material, rPLA and rPETG (reference materials)

PROBLEM DEFINITION **

Limit and define the scope and solution space of your project to one that is manageable within one Master Graduation Project of 30 EC (= 20 full time weeks or 100 working days) and clearly indicate what issue(s) should be addressed in this project.

As explained in the introduction there is a need for a material (mix) that is suitable for FDM/FFF printing and serves as an alternative to commonly used filaments, while being less reliant on non-renewable and valuable resources. In this graduation project, several material recipes will be developed and tested. Successful prints will be rated on 6 key elements: print-ability, dimensional accuracy, print resolution, surface finish, price and environmental impact. Although commonly used filaments are well-known for their mechanical properties, testing the successful prints made with the various material recipes on mechanical properties will be omitted from this research due to the limited time that is available.

In the flow chart above, the development & testing procedure of material recipes is detailed. The main challenges that will be tackled throughout this project are:

1. Develop and iterate on various material recipes which will be used to print with
2. Adjusting a 'standard' FDM/FFF machine to enable it to print with paste-like material mixes. The printed materials will be the material recipes mentioned at point 1.
3. Analyze the prints and rate them on print-ability, dimensional accuracy, resolution, surface finish, price, and environmental impact.

The goal is to find material mixes that scores similarly well or better on the mentioned criteria. An exploratory search will be done for material mixes that fail to meet every criterion, but yield successful prints in order to find a use case and target audience that fits the material mix's properties.

ASSIGNMENT **

State in 2 or 3 sentences what you are going to research, design, create and / or generate, that will solve (part of) the issue(s) pointed out in "problem definition". Then illustrate this assignment by indicating what kind of solution you expect and / or aim to deliver, for instance: a product, a product-service combination, a strategy illustrated through product or product-service combination ideas, ... In case of a Specialisation and/or Annotation, make sure the assignment reflects this/these.

The goal in this research is to find one or more material mixes that are suitable for FDM/FFF printing, give similar or better print results than rPLA & rPETG (in FDM/FFF), while being less reliant on non-renewable and valuable resources.

The focus of this project will be on the development of material mixes that form paste-like substances that are suitable for FDM/FFF printing. A standard FFF machine will be altered to enable printing with these paste-like materials. Successful prints will depend as much on printer modification as material mixes, so this will also be a significant part of the project work.

The prints will be assessed on print-ability, dimensional accuracy, resolution, surface finish, price and (if time allows it) environmental impact. Due to limited time available, mechanical properties fall out of the scope of this research.

The aim is to find one or more material mixes that deliver similar or better print results than the reference materials, rPLA and rPTEG (manufactured by the client), while being less reliant on non-renewable and valuable resources.

For material mixes that leads to successful prints, a suitable use case & target user will be explored. A material mix may not need to match the reference materials to be a suitable replacement in specific use cases.

Initials & Name E.J. Donders Student number 4214862

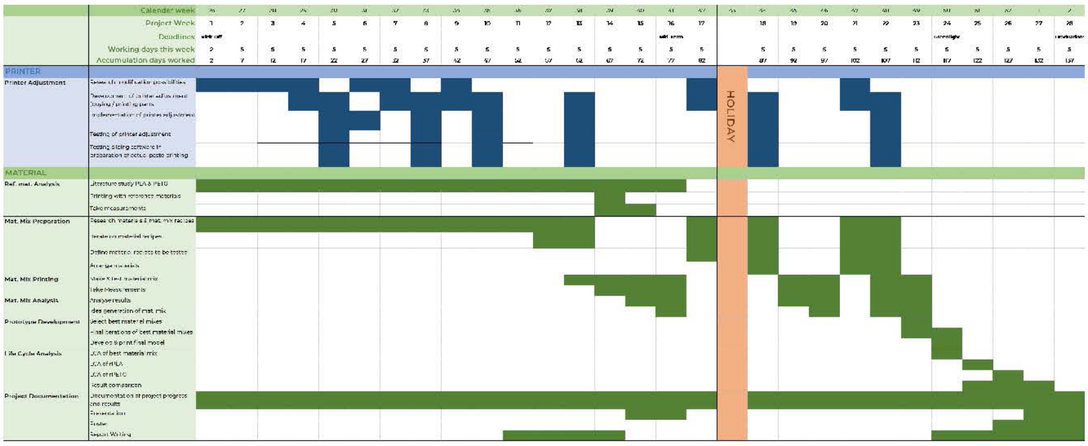
Title of Project Using materials derived from waste streams for 3D Printing

PLANNING AND APPROACH **

Include a Gantt Chart (replace the example below - more examples can be found in Manual 2) that shows the different phases of your project, deliverables you have in mind, meetings, and how you plan to spend your time. Please note that all activities should fit within the given net time of 30 EC = 20 full time weeks or 100 working days, and your planning should include a kick-off meeting, mid-term meeting, green light meeting and graduation ceremony. Illustrate your Gantt Chart by, for instance, explaining your approach, and please indicate periods of part-time activities and/or periods of not spending time on your graduation project, if any, for instance because of holidays or parallel activities.

start date 30 - 6 - 2021

30 - 11 - 2021 end date



The first part of the project has been used to further investigate previous research about developing paste-like material mixes for 3D printing and for collection and developing material recipes that can be tested within this project. Also, a considerable amount of time was spent on researching and developing adjustments for the printer so it could print with these paste-like materials. Several problems were met while adjusting the printer which had to be dealt with in order to be able to successfully print. This also explains why the project takes longer than the goal of 100 days.

In the step that followed further research was done into the reference materials to have better understanding about their reliance on non-renewable and valuable resources throughout their lifecycle as well as their End-of-Life scenarios. In week 38 the projects focus moves over to testing the material mixes. For several weeks an iterative process will be gone through in which recipes will be defined, tested and analyzed. This will be a lot of trial and error to find what works and what doesn't. Interesting intermediate results will be discussed with the stakeholders and experts involved in the project.

In the 23th week of the project of the final and winning material recipes will be determined based on print-ability, dimensional accuracy, resolution, surface finish and price and environmental impact of the successful prints . Any final tweaks of the material recipe will be done to further improve it. If time allows it, a LCA will done.

The last three weeks will be used to draft final conclusions of the project, reflect on how the project has proceeded, set up recommendations for further research and prepare the final presentation for the project.

MOTIVATION AND PERSONAL AMBITIONS

Explain why you set up this project, what competences you want to prove and learn. For example: acquired competences from your MSc programme, the elective semester, extra-curricular activities (etc.) and point out the competences you have yet developed. Optionally, describe which personal learning ambitions you explicitly want to address in this project, on top of the learning objectives of the Graduation Project, such as: in depth knowledge a on specific subject, broadening your competences or experimenting with a specific tool and/or methodology, ... Stick to no more than five ambitions.

This project caters to two large interests of me: sustainability and 3D printing. I've been fascinated by the possibilities of 3D printing since high-school and have recently made the step to purchase my own 3D printer. However, the sustainability concerns of 3D printing weigh heavy on my mind and this project offers a great opportunity to develop a less environmentally detrimental application of the technology.

Throughout this project I will need to further develop skills that have been touched upon in the different courses and projects that I have done since I started my studies.
I look forward to learning a lot more about coding and working with electronics, both of which will be needed to alter a standard FFF printer to be able to print with paste-like materials.
Furthermore, I am excited about learning more about materials, gaining the knowledge to develop material recipes to test with FFF printing.

My main passion is photography and I would like to harness this passion, and the skills that I've developed through it, to clearly visualize the process, progress and results of this project. This project is an opportunity to further develop my photography skills by focusing on clear communication of the technological development that will take place throughout the project.

On top of that, this project allows me to further develop my skills in critical analysis of literature that is used as reference and my own results. Development of these skills will help me to improve my scientific discussion to verify the validity of the research and results. Communicating the intermediate and final results of the research with the involved parties will allow me to further develop my presentation skills.

FINAL COMMENTS

In case your project brief needs final comments, please add any information you think is relevant.

Appendix B - Specimen Measurement Chart

Sample Name	Length 1 (mm)	Length 2 (mm)	Length 3 (mm)	Height 1 (mm)	Height 2 (mm)	Height 3 (mm)	Width 1 (mm)	Width 2 (mm)	Width 3 (mm)	Length Average (mm)	Height Average (mm)	Width Average (mm)
rPLA specimen 1	58.30	58.33	58.31	4.06	4.07	4.07	9.81	9.82	9.81	**58.31**	**4.07**	**9.81**
rPLA specimen 2	58.12	58.14	58.12	4.05	4.06	4.05	9.92	9.93	9.92	**58.13**	**4.05**	**9.92**
rPLA specimen 3	58.11	58.11	58.12	4.05	4.04	4.04	9.84	9.85	9.85	**58.11**	**4.04**	**9.85**
rPLA specimen 4	58.18	58.19	58.19	4.03	4.03	4.03	9.90	9.90	9.90	**58.19**	**4.03**	**9.90**
rPLA specimen 5	58.20	58.21	58.21	4.03	4.03	4.02	9.79	9.83	9.82	**58.21**	**4.03**	**9.81**
rPLA specimen 6	58.21	58.22	58.19	4.03	4.03	4.02	9.87	9.87	9.87	**58.21**	**4.03**	**9.87**
rPLA specimen 7	58.24	58.26	58.24	4.07	4.07	4.06	9.89	9.86	9.86	**58.25**	**4.07**	**9.87**
rPLA specimen 8	58.11	58.08	58.10	4.04	4.03	4.04	9.79	9.81	9.80	**58.10**	**4.04**	**9.80**
rPLA specimen 9	58.24	58.25	58.21	4.06	4.05	4.05	9.92	9.92	9.92	**58.23**	**4.05**	**9.92**
rPLA specimen 10	58.33	58.37	58.33	4.14	4.13	4.13	9.98	9.97	9.97	**58.34**	**4.13**	**9.97**
rPLA specimen 11	58.24	58.26	58.23	4.02	4.05	4.05	9.84	9.83	9.83	**58.24**	**4.04**	**9.83**
rPLA AVERAGE										**58.21**	**4.05**	**9.87**
rPETG specimen 1	58.33	58.29	58.31	3.98	3.97	3.98	9.88	9.88	9.89	**58.31**	**3.98**	**9.88**
rPETG specimen 2	58.28	58.28	58.30	3.99	3.98	3.98	9.90	9.89	9.88	**58.29**	**3.98**	**9.89**
rPETG specimen 3	58.31	58.29	58.29	4.00	4.00	4.00	9.84	9.86	9.82	**58.30**	**4.00**	**9.84**
rPETG specimen 4	58.26	58.27	58.26	3.97	3.97	3.97	9.88	9.87	9.87	**58.26**	**3.97**	**9.87**
rPETG specimen 5	58.22	58.23	58.22	4.00	4.00	3.99	9.90	9.90	9.90	**58.22**	**4.00**	**9.90**
rPETG specimen 6	58.30	58.30	58.29	3.98	3.99	3.99	9.85	9.85	9.85	**58.30**	**3.99**	**9.85**
rPETG AVERAGE										**58.28**	**3.99**	**9.87**
Material Mix specimen 1	57.80	57.83	57.80	3.54	3.51	3.51	9.39	9.40	9.40	**57.81**	**3.52**	**9.40**
Material Mix specimen 2	57.38	57.36	57.40	3.81	3.81	3.82	9.44	9.48	9.47	**57.38**	**9.81**	**9.46**
Material Mix specimen 3	57.16	57.14	57.12	3.84	3.78	3.79	9.30	9.27	9.32	**57.14**	**3.80**	**9.30**
Material Mix specimen 4	57.15	57.11	57.20	3.92	3.90	3.90	9.44	9.38	9.34	**57.15**	**3.91**	**9.39**
Material Mix specimen 5	57.28	57.26	57.22	3.81	3.81	3.82	9.68	9.65	9.63	**57.25**	**3.81**	**9.65**
Material Mix specimen 6	57.68	57.65	57.59	3.75	3.75	3.74	9.52	9.51	9.51	**57.64**	**3.75**	**9.51**
Material Mix specimen 7	57.54	57.56	57.53	3.77	3.77	3.77	9.26	9.27	9.28	**57.54**	**3.77**	**9.27**
Material Mix AVERAGE										**57.42**	**3.77**	**9.43**

Appendix C - Specimen Size Deviation

Sample Name	Length Average (mm)	Height Average (mm)	Width Average (mm)	Length CAD (mm)	Height CAD (mm)	Width CAD (mm)	Length Deviation (mm)	Height Deviation (mm)	Width Deviation (mm)	Length Deviation (%)	Height Deviation (%)	Width Deviation (%)
rPLA specimen 1	*58.31*	*4.07*	*9.81*	*58.40*	*4.00*	*9.90*	*-0.09*	*0.07*	*-0.09*	*-0.15*	*1.67*	*-0.88*
rPLA specimen 2	*58.13*	*4.05*	*9.92*	*58.40*	*4.00*	*9.90*	*-0.27*	*0.05*	*0.02*	*-0.47*	*1.33*	*0.24*
rPLA specimen 3	*58.11*	*4.04*	*9.85*	*58.40*	*4.00*	*9.90*	*-0.29*	*0.04*	*-0.05*	*-0.49*	*1.08*	*-0.54*
rPLA specimen 4	*58.19*	*4.03*	*9.90*	*58.40*	*4.00*	*9.90*	*-0.21*	*0.03*	*0.00*	*-0.37*	*0.75*	*0.00*
rPLA specimen 5	*58.21*	*4.03*	*9.81*	*58.40*	*4.00*	*9.90*	*-0.19*	*0.03*	*-0.09*	*-0.33*	*0.67*	*-0.88*
rPLA specimen 6	*58.21*	*4.03*	*9.87*	*58.40*	*4.00*	*9.90*	*-0.19*	*0.03*	*-0.03*	*-0.33*	*0.67*	*-0.30*
rPLA specimen 7	*58.25*	*4.07*	*9.87*	*58.40*	*4.00*	*9.90*	*-0.15*	*0.07*	*-0.03*	*-0.26*	*1.67*	*-0.30*
rPLA specimen 8	*58.10*	*4.04*	*9.80*	*58.40*	*4.00*	*9.90*	*-0.30*	*0.04*	*-0.10*	*-0.52*	*0.92*	*-1.01*
rPLA specimen 9	*58.23*	*4.05*	*9.92*	*58.40*	*4.00*	*9.90*	*-0.17*	*0.05*	*-0.02*	*-0.29*	*1.33*	*0.20*
rPLA specimen 10	*58.34*	*4.13*	*9.97*	*58.40*	*4.00*	*9.90*	*-0.06*	*0.01*	*0.07*	*-0.10*	*3.33*	*0.74*
rPLA specimen 11	*58.24*	*4.04*	*9.83*	*58.40*	*4.00*	*9.90*	*-0.16*	*0.04*	*-0.07*	*-0.27*	*1.00*	*-0.67*
rPLA AVERAGE	**58.21**	**4.05**	**9.87**	**58.40**	**4.00**	**9.90**	**-0.19**	**0.05**	**-0.03**	**-0.32**	**1.31**	**-0.31**
rPETG specimen 1	*58.31*	*3.98*	*9.88*	*58.40*	*4.00*	*9.90*	*-0.09*	*-0.02*	*-0.02*	*-0.15*	*-0.58*	*-0.17*
rPETG specimen 2	*58.29*	*3.98*	*9.89*	*58.40*	*4.00*	*9.90*	*-0.11*	*-0.02*	*-0.01*	*-0.19*	*-0.42*	*-0.10*
rPETG specimen 3	*58.30*	*4.00*	*9.84*	*58.40*	*4.00*	*9.90*	*-0.10*	*0.00*	*-0.06*	*-0.18*	*0.00*	*-0.61*
rPETG specimen 4	*58.26*	*3.97*	*9.87*	*58.40*	*4.00*	*9.90*	*-0.14*	*-0.03*	*-0.03*	*-0.23*	*-0.75*	*-0.27*
rPETG specimen 5	*58.22*	*4.00*	*9.90*	*58.40*	*4.00*	*9.90*	*-0.18*	*0.00*	*0.00*	*-0.30*	*-0.08*	*0.00*
rPETG specimen 6	*58.30*	*3.99*	*9.85*	*58.40*	*4.00*	*9.90*	*-0.10*	*-0.01*	*-0.05*	*-0.18*	*-0.33*	*-0.51*
rPETG AVERAGE	**58.28**	**3.99**	**9.87**	**58.40**	**4.00**	**9.90**	**-0.12**	**-0.01**	**-0.03**	**-0.21**	**-0.36**	**-0.27**
Material Mix specimen 1	*57.81*	*3.52*	*9.40*	*58.40*	*4.00*	*9.90*	*-0.59*	*-0.48*	*-0.50*	*-1.01*	*-12.00*	*-5.08*
Material Mix specimen 2	*57.38*	*9.81*	*9.46*	*58.40*	*4.00*	*9.90*	*-1.02*	*-0.19*	*-0.44*	*-1.75*	*-4.67*	*-4.41*
Material Mix specimen 3	*57.14*	*3.80*	*9.30*	*58.40*	*4.00*	*9.90*	*-1.26*	*-0.20*	*-0.60*	*-2.16*	*-4.92*	*-6.09*
Material Mix specimen 4	*57.15*	*3.91*	*9.39*	*58.40*	*4.00*	*9.90*	*-1.25*	*-0.09*	*-0.51*	*-2.13*	*-2.33*	*-5.19*
Material Mix specimen 5	*57.25*	*3.81*	*9.65*	*58.40*	*4.00*	*9.90*	*-1.15*	*-0.19*	*-0.25*	*-1.96*	*-4.67*	*-2.49*
Material Mix specimen 6	*57.64*	*3.75*	*9.51*	*58.40*	*4.00*	*9.90*	*-0.76*	*-0.25*	*-0.39*	*-1.30*	*-6.33*	*-3.91*
Material Mix specimen 7	*57.54*	*3.77*	*9.27*	*58.40*	*4.00*	*9.90*	*-0.86*	*-0.23*	*-0.63*	*-1.47*	*-5.75*	*-6.36*
Material Mix AVERAGE	**57.42**	**3.77**	**9.43**	**58.40**	**4.00**	**9.90**	**-0.98**	**-0.23**	**-0.47**	**-1.68**	**-5.81**	**-4.79**

Appendix D - Specimen Volume, Weight & Density

Sample Name	Length Average (mm)	Height Average (mm)	Width Average (mm)	Print Volume (mm³)	Print Volume (cm³)	Print Weight (g)	Density (g/cm³)	Official Density (g/cm³)	Density Deviation (g/cm³)	Density Deviation (%)
rPLA specimen 1	*58.31*	*4.07*	*9.81*	*2327.14259*	*2.32714259*	*2.7*	*1.16*	*1.24*	*-0.08*	*-6.43*
rPLA specimen 2	*58.13*	*4.05*	*9.92*	*2338.004371*	*2.338004371*	*2.7*	*1.15*	*1.24*	*-0.09*	*-6.87*
rPLA specimen 3	*58.11*	*4.04*	*9.85*	*2313.686803*	*2.313686803*	*2.7*	*1.17*	*1.24*	*-0.07*	*-5.89*
rPLA specimen 4	*58.19*	*4.03*	*9.90*	*2321.47344*	*2.32147344*	*2.6*	*1.12*	*1.24*	*-0.12*	*-9.68*
rPLA specimen 5	*58.21*	*4.03*	*9.81*	*2300.037727*	*2.300037727*	*2.7*	*1.17*	*1.24*	*-0.07*	*-5.33*
rPLA specimen 6	*58.21*	*4.03*	*9.87*	*2313.319195*	*2.313319195*	*2.7*	*1.17*	*1.24*	*-0.07*	*-5.87*
rPLA specimen 7	*58.25*	*4.07*	*9.87*	*2337.904707*	*2.337904707*	*2.7*	*1.15*	*1.24*	*-0.09*	*-6.86*
rPLA specimen 8	*58.10*	*4.04*	*9.80*	*2298.265402*	*2.298265402*	*2.7*	*1.17*	*1.24*	*-0.07*	*-5.26*
rPLA specimen 9	*58.23*	*4.05*	*9.92*	*2341.507982*	*2.341507982*	*2.7*	*1.15*	*1.24*	*-0.09*	*-7.01*
rPLA specimen 10	*58.34*	*4.13*	*9.97*	*2405.093713*	*2.405093713*	*2.7*	*1.12*	*1.24*	*-0.12*	*-9.47*
rPLA specimen 11	*58.24*	*4.04*	*9.83*	*2313.813489*	*2.313813489*	*2.7*	*1.17*	*1.24*	*-0.07*	*-5.89*
rPLA AVERAGE	**58.21**	**4.05**	**9.87**	**2328.131516**	**2.328131516**	**2.69**	**1.16**	**1.24**	**-0.08**	**-6.79**
rPETG specimen 1	*58.31*	*3.98*	*9.88*	*2299.149277*	*2.299149277*	*2.7*	*1.18*	*1.27*	*-0.09*	*-7.23*
rPETG specimen 2	*58.29*	*3.98*	*9.89*	*2311.288861*	*2.311288861*	*2.7*	*1.18*	*1.27*	*-0.09*	*-7.41*
rPETG specimen 3	*58.30*	*4.00*	*9.84*	*2298.783701*	*2.298783701*	*2.7*	*1.18*	*1.27*	*-0.09*	*-7.35*
rPETG specimen 4	*58.26*	*3.97*	*9.87*	*2303.124281*	*2.303124281*	*2.7*	*1.18*	*1.27*	*-0.09*	*-6.91*
rPETG specimen 5	*58.22*	*4.00*	*9.90*	*2294.81626*	*2.29481626*	*2.7*	*1.17*	*1.27*	*-0.10*	*-7.72*
rPETG specimen 6	*58.30*	*3.99*	*9.85*	*2319.098369*	*2.319098369*	*2.7*	*1.18*	*1.27*	*-0.09*	*-7.13*
rPETG AVERAGE	**58.28**	**3.99**	**9.87**	**2304.412982**	**2.304412982**	**2.7**	**1.18**	**1.27**	**-0.09**	**-7.29**
Material Mix specimen 1	*57.81*	*3.52*	*9.40*	*1912.138976*	*1.912138976*	*2.7*	*1.41*	-	-	-
Material Mix specimen 2	*57.38*	*9.81*	*9.46*	*2070.663134*	*2.070663134*	*3.1*	*1.50*	-	-	-
Material Mix specimen 3	*57.14*	*3.80*	*9.30*	*2020.374532*	*2.020374532*	*3.0*	*1.48*	-	-	-
Material Mix specimen 4	*57.15*	*3.91*	*9.39*	*2095.845755*	*2.095845755*	*3.1*	*1.48*	-	-	-
Material Mix specimen 5	*57.25*	*3.81*	*9.65*	*2107.574082*	*2.107574082*	*3.1*	*1.47*	-	-	-
Material Mix specimen 6	*57.64*	*3.75*	*9.51*	*2054.479172*	*2.054479172*	*3.0*	*1.46*	-	-	-
Material Mix specimen 7	*57.54*	*3.77*	*9.27*	*2011.018659*	*2.011018659*	*3.1*	*1.54*	-	-	-
Material Mix AVERAGE	**57.42**	**3.77**	**9.43**	**2039.026325**	**2.039026325**	**3.01**	**1.48**	**-**	**-**	**-**

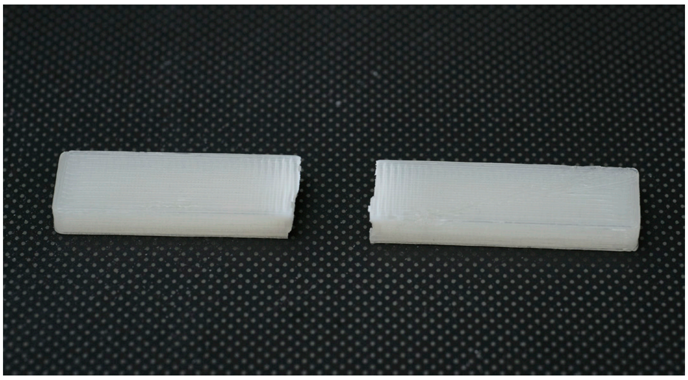
Appendix E - Bending Tests Results

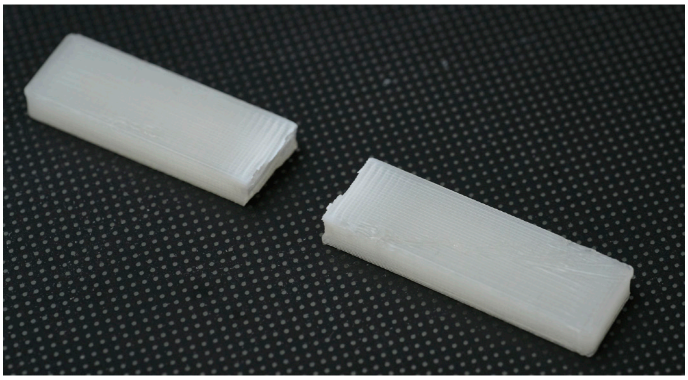
Sample Name	F_{max} (N)	dL at F_{max} (mm)	F_{break} (N)	dL at break (mm)	W to F_{max} (N*mm)	a_0 (mm)	b_0 (mm)	s_0 (mm^2)	t_{test} (s)
rPLA specimen 1	-	-	-	-	-	-	-	-	-
rPLA specimen 2	247.9984283	4.211464405	120.4513626	4.534096241	603.8367654	4.07	9.81	39.9267	6.14
rPLA specimen 3	245.3592072	4.198077679	118.3490067	5.603155136	604.6564218	4.04	9.85	39.794	7.44
rPLA specimen 4	247.2142334	4.213207722	121.5553818	4.728359699	600.8669163	4.03	9.9	39.897	6.368
rPLA specimen 5	243.7803955	4.177662373	117.4071808	4.770643711	587.4245023	4.03	9.81	39.5343	6.428
rPLA specimen 6	247.0296783	4.314652443	121.900589	4.817912102	621.0739619	4.03	9.87	39.7761	6.478
rPLA specimen 7	245.2906494	4.220014095	120.1752853	4.70802021	600.8740757	4.07	9.87	40.1709	6.356
rPLA specimen 8	235.8760376	4.086452007	114.7072144	5.429458141	559.5068259	4.04	9.8	39.592	7.234
rPLA specimen 9	247.2076569	4.230065823	121.625824	4.522441864	604.9566376	4.05	9.92	40.176	6.1
rPLA specimen 10	255.0652161	4.371898651	123.6005783	5.414152622	669.2114992	4.13	9.97	41.1761	7.216
rPLA specimen 11	243.5378265	4.326414585	119.5166016	5.816264629	627.3793417	4.04	9.83	39.7132	7.648
rPLA AVERAGE	**245.8359329**	**4.234990978**	**120.451363**	**5.03445044**	**607.978695**	**4.053**	**9.863**	**39.97563**	**6.7408**
rPETG specimen 1	214.2875214	11.83582211	107.3369293	15.2513504	1478.384867	4.98	9.88	49.2024	18.82
rPETG specimen 2	182.7601624	11.17513275	91.36968231	13.45493126	1340.515777	3.98	9.89	39.3622	16.702
rPETG specimen 3	214.2875214	11.94583225	107.135025	13.67968655	1478.137781	4	9.84	39.36	16.972
rPETG specimen 4	178.0677643	11.77505112	88.57182312	15.29371452	1374.981668	3.97	9.87	39.1839	18.88
rPETG specimen 5	211.0278015	11.81224442	105.5078583	16.25355339	1490.925292	4	9.9	39.6	20.034
rPETG specimen 6	190.5063782	11.44388866	95.24023438	13.93313599	1359.482778	3.99	9.85	39.3015	17.262
rPETG AVERAGE	**198.5898997**	**11.66466188**	**99.1935921**	**14.6443954**	**1420.40469**	**4.153333**	**9.871667**	**41.00167**	**18.11167**
Material Mix specimen 1	6.991416454	0.741231143	5.791919231	0.845769107	2.924785732	3.52	9.4	33.088	1.734
Material Mix specimen 2	8.939803123	1.005129099	8.463057518	1.026209116	5.424124625	3.81	9.46	36.0426	1.938
Material Mix specimen 3	7.290241718	0.767481565	6.739590168	0.819506407	2.968492546	3.8	9.3	35.34	1.694
Material Mix specimen 4	9.269721031	0.691012025	7.342519283	0.847529054	3.172761961	3.91	9.39	36.7149	1.742
Material Mix specimen 5	9.567864418	0.776045978	9.25405407	0.807486713	3.817659855	3.81	9.65	36.7665	1.69
Material Mix specimen 6	9.208846092	0.79188931	8.895445824	0.823207974	4.199897342	3.75	9.51	35.6625	1.726
Material Mix specimen 7	8.453934669	0.764092028	7.93083477	0.816223681	3.85913543	3.77	9.27	34.9479	1.704
Material Mix AVERAGE	**8.531689644**	**0.790983021**	**7.77391727**	**0.85513315**	**3.76669393**	**3.767143**	**9.425714**	**35.50891**	**1.746857**

Appendix F - Bending Specimen Photos

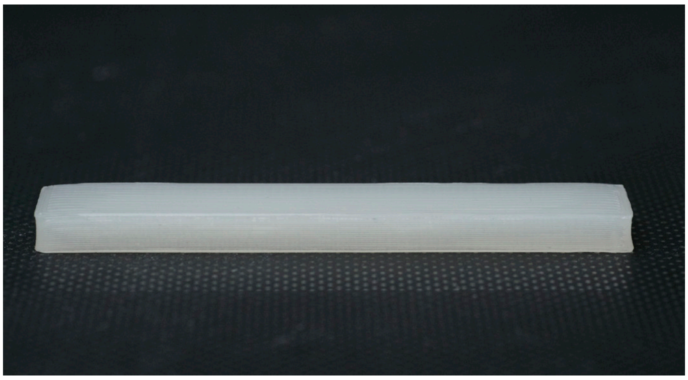
rPLA specimens

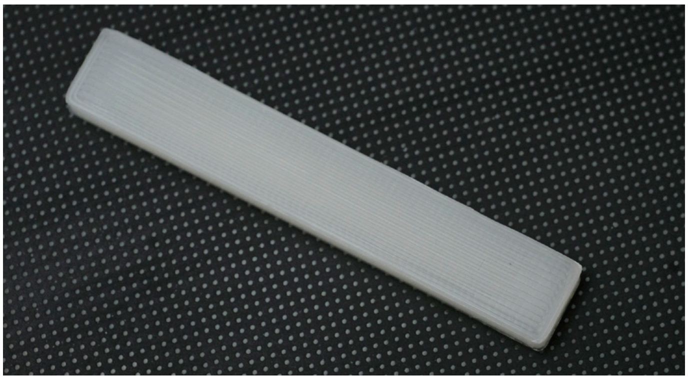
rPLA specimen 1



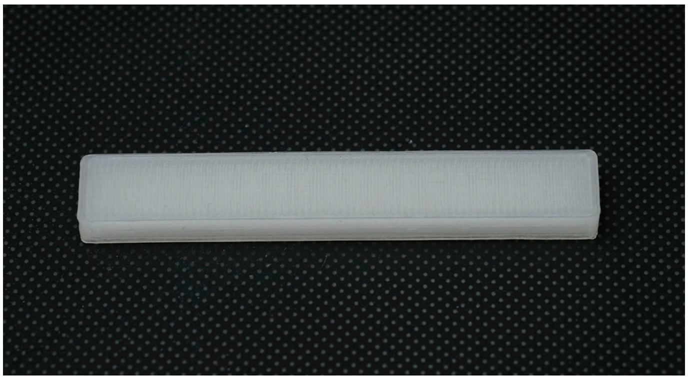


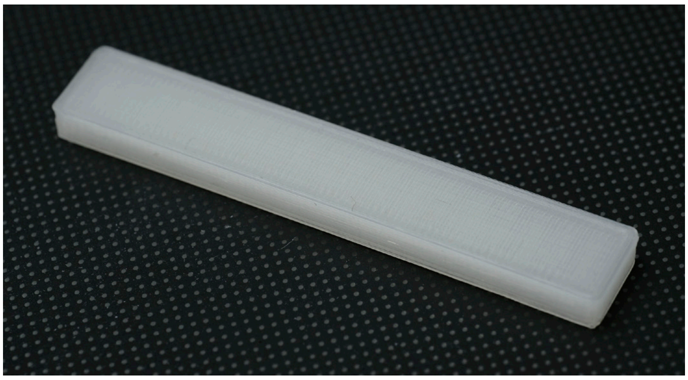
rPLA specimen 2



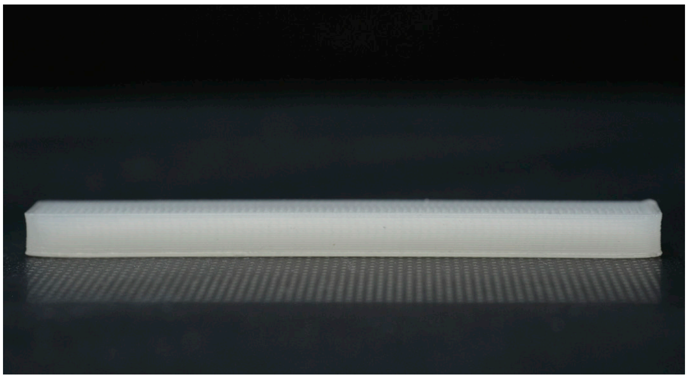


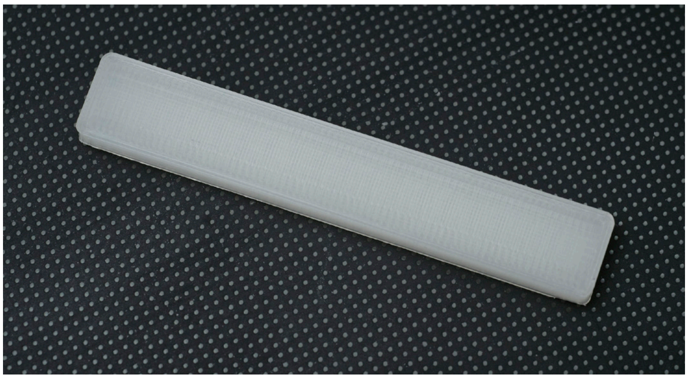
rPLA specimen 3



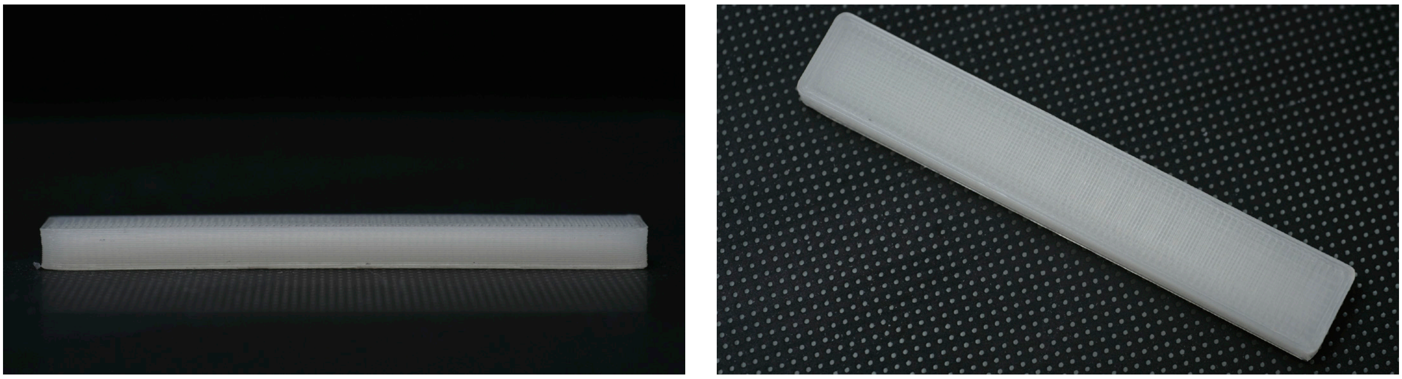


rPLA specimen 4

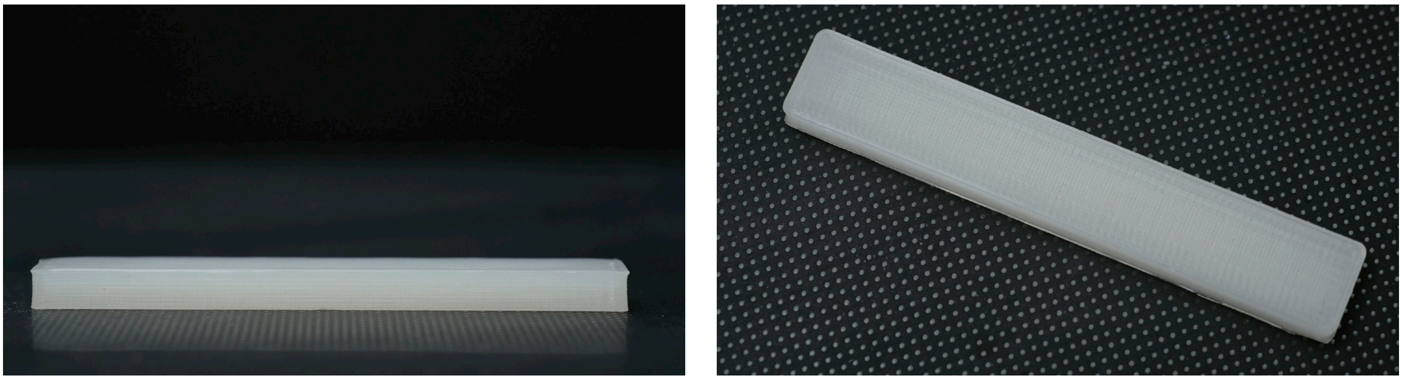




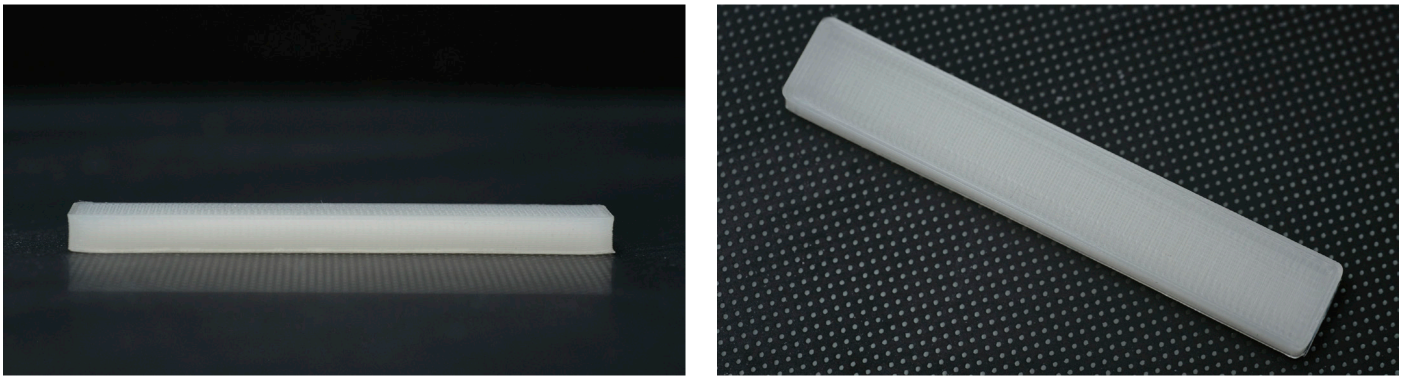
rPLA specimen 5



rPLA specimen 6



rPLA specimen 7



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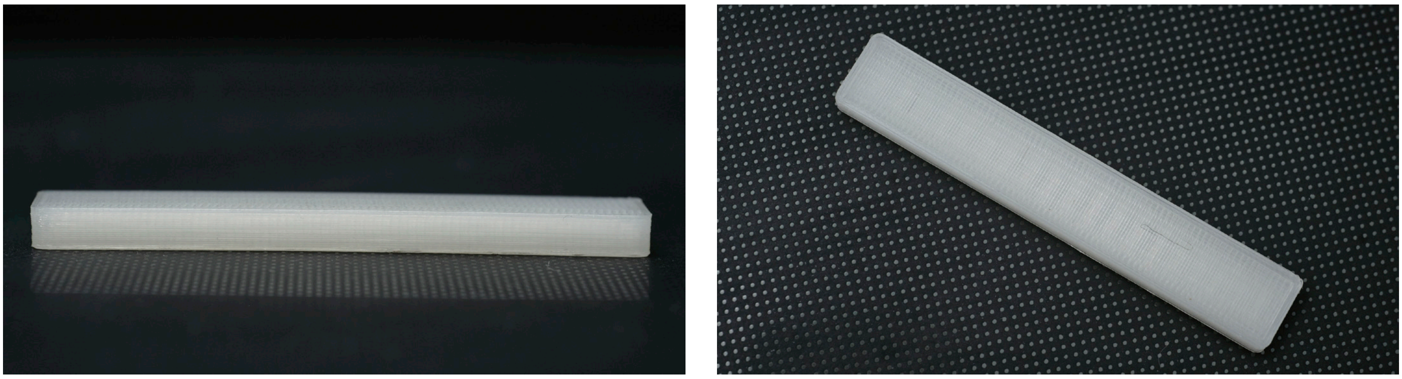
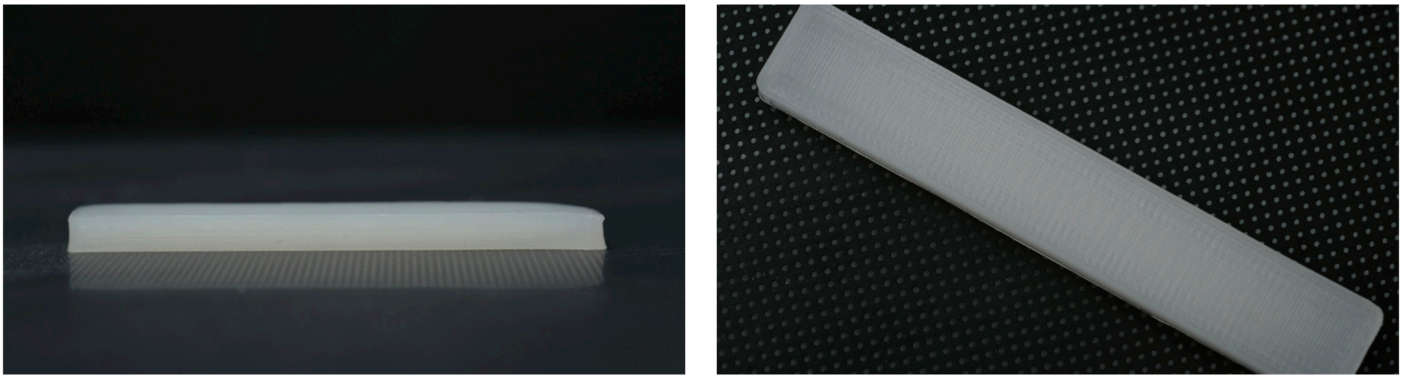


rPLA specimen 9



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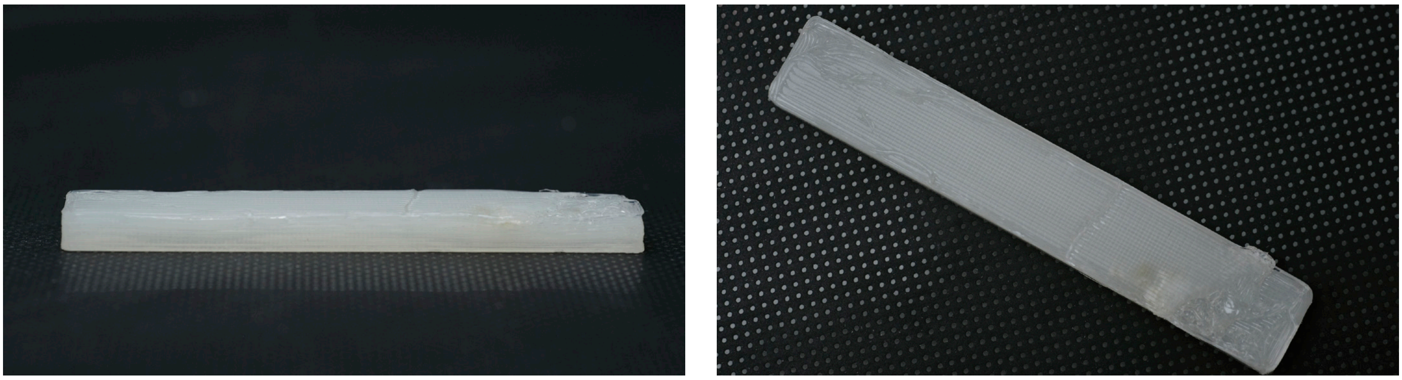
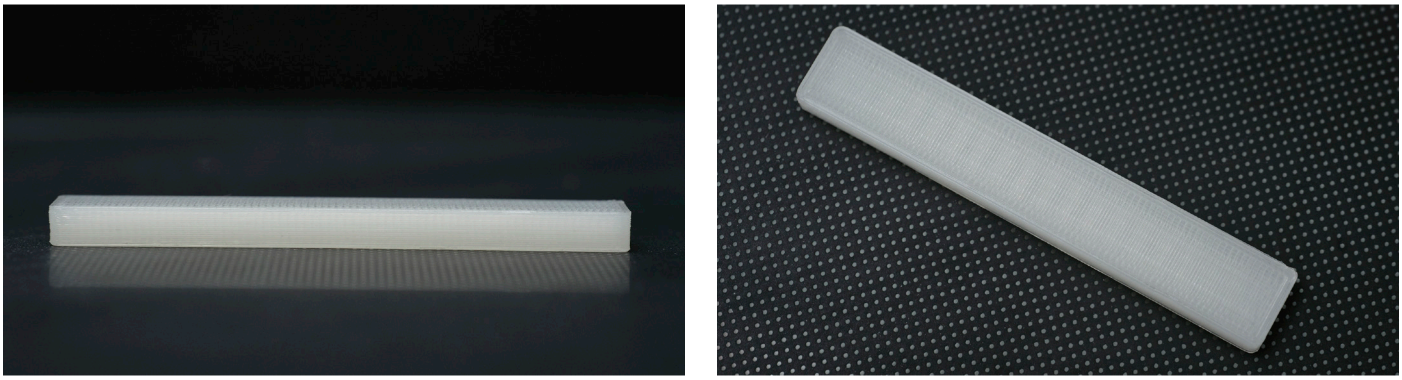
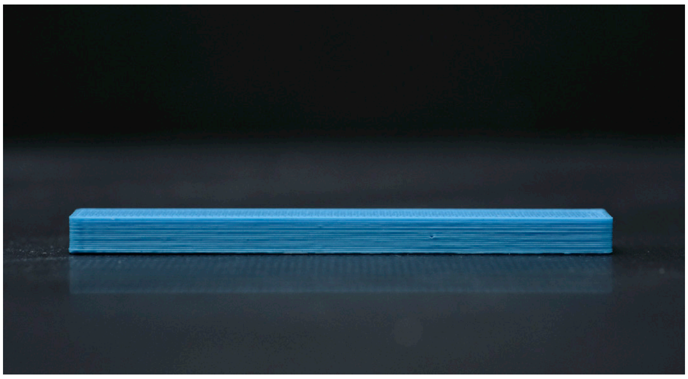


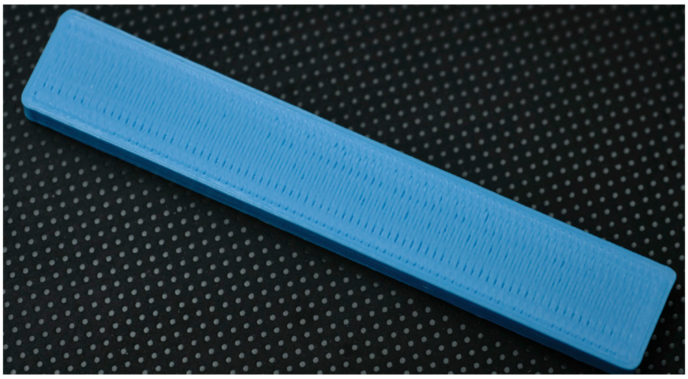
rPLA specimen 11



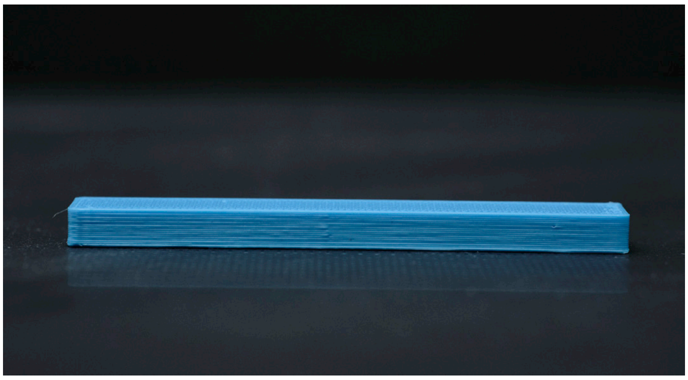
rPETG specimens

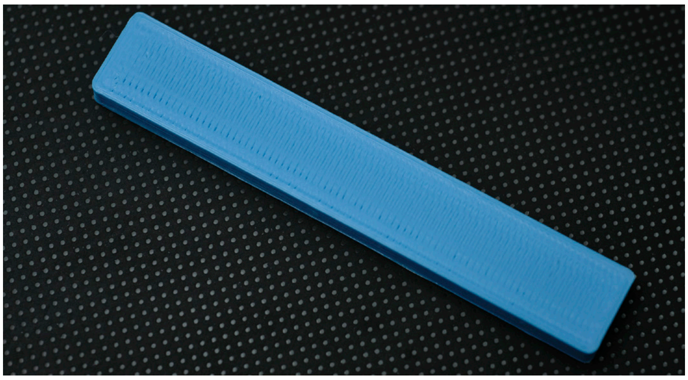
rPETG specimen 1



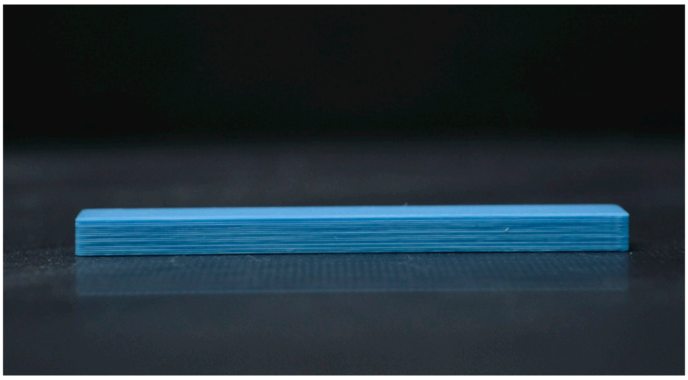


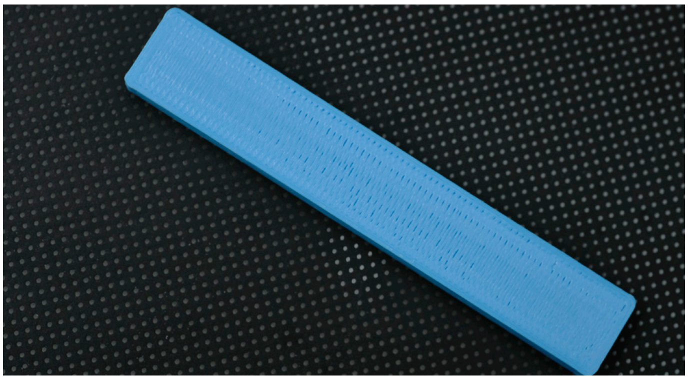
rPETG specimen 2



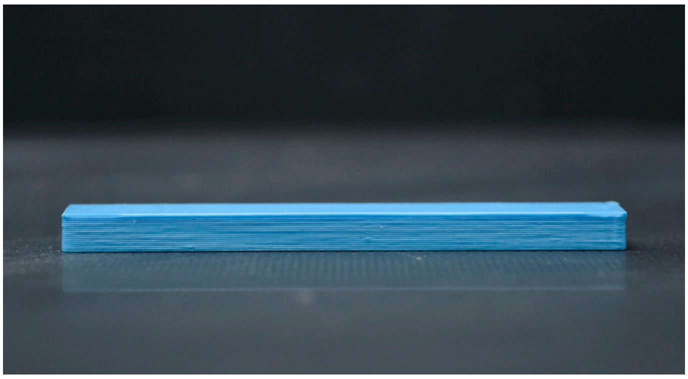


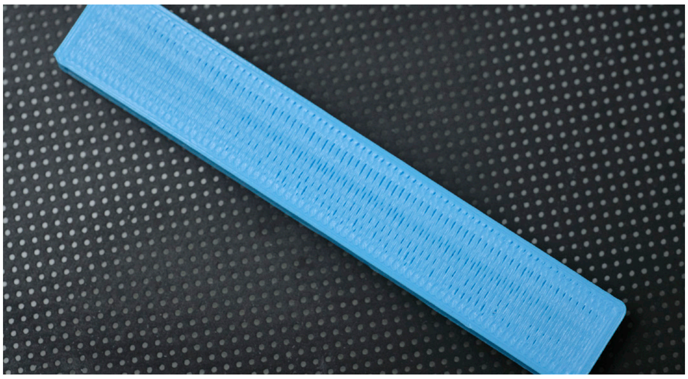
rPETG specimen 3



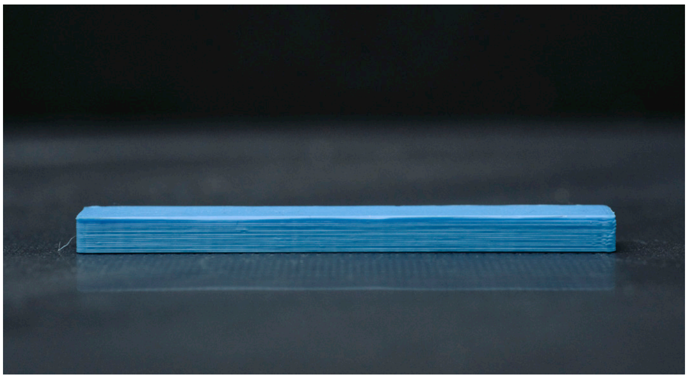


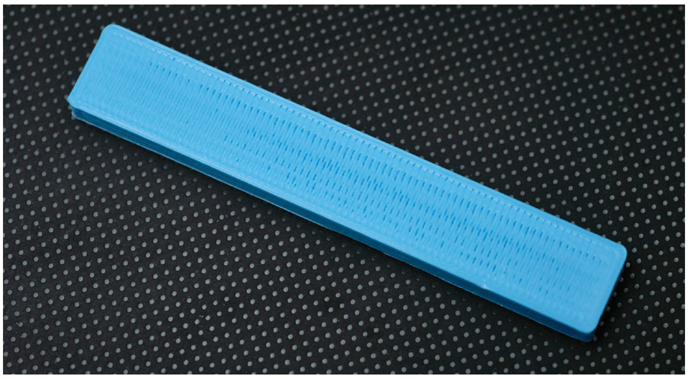
rPETG specimen 4



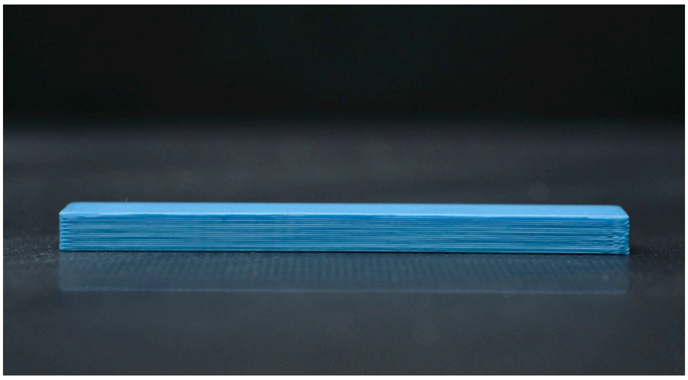


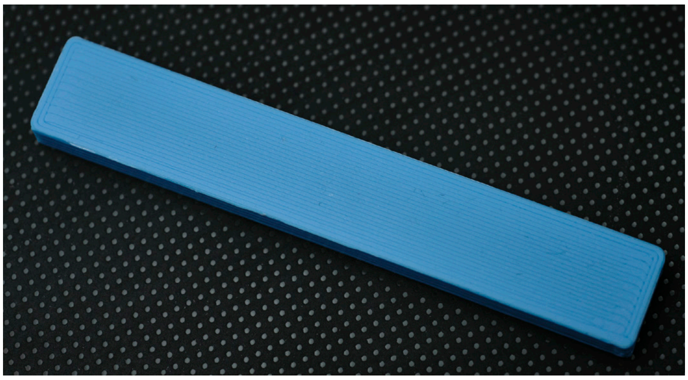
rPETG specimen 5





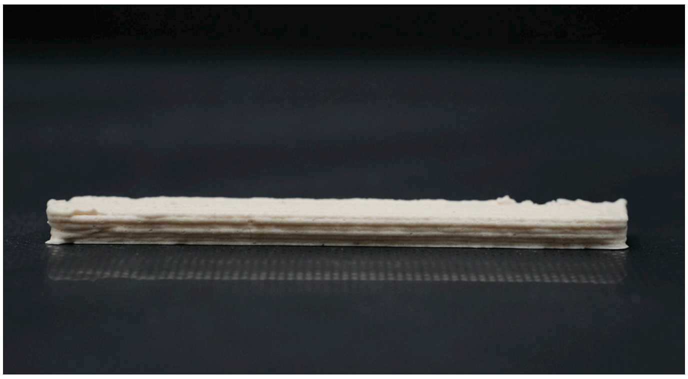
rPETG specimen 6

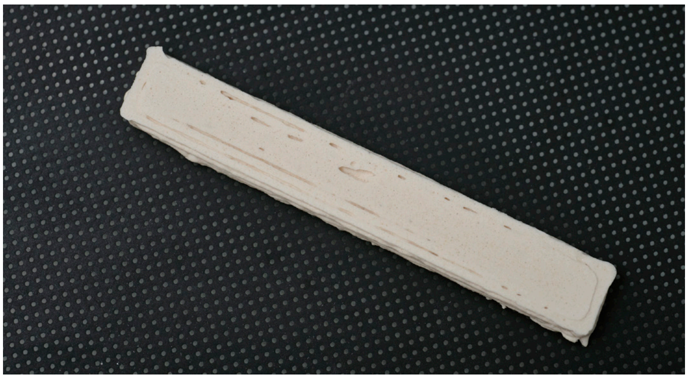




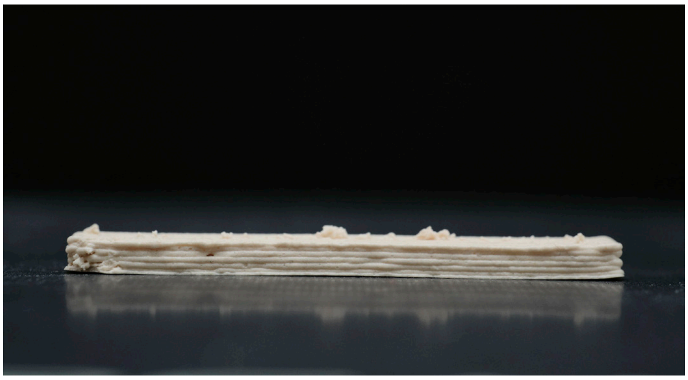
Material Mix specimens

Material Mix specimen 1

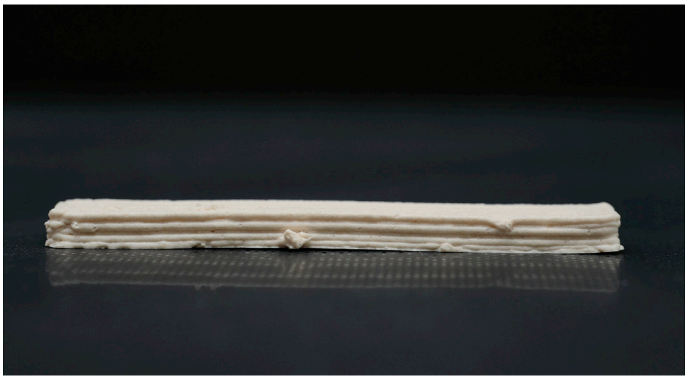


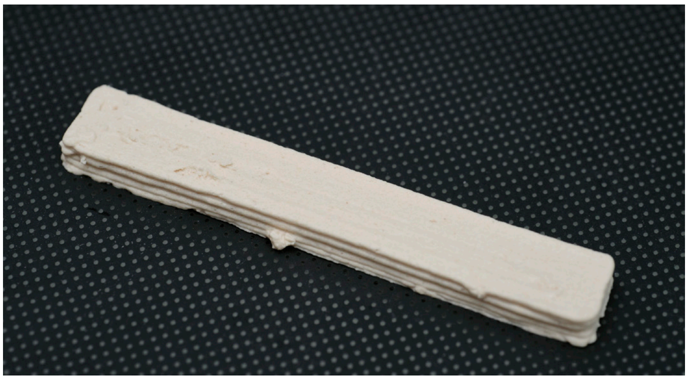


Material Mix specimen 2

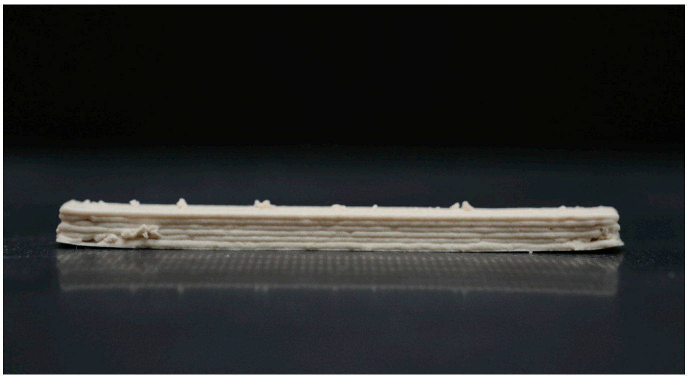


Material Mix specimen 3





Material Mix specimen 4



Material Mix specimen 5

Material Mix specimen 6

Material Mix specimen 7

Appendix G - Download links

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