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FEUP FACULDADE DE ENGENHARIA
UNIVERSIDADE DO PORTO

3D PRINTED NEGATIVE MOULDS FOR SOFT LITHOGRAPHY MICROFLUIDICS

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MASTER THESIS IN CHEMICAL ENGINEERING
PRESENTED TO THE FACULTY OF ENGINEERING
OF THE UNIVERSITY OF PORTO

Master in Chemical Engineering

3D Printed Negative Moulds for Soft Lithography Microfluidics

Master Thesis

of

Carlos Miguel Sousa Loureiro

Developed within the course of dissertation

held in

Associated Laboratory in Chemical Engineering

/ Transport Phenomena Research Center

Supervisor at FEUP: **Prof. Francisco José Galindo Rosales**

March 2025

Acknowledgment

This dissertation would not have been possible without the guidance and support of my supervisor, Dr. Francisco José Galindo Rosales that I would like to express my gratitude and appreciation.

Also, I am grateful for the team of Transport Phenomena Research Center (CEFT) for the laboratory and machine access, the space and materials provided for this work and the kind support throughout this journey.

Carlos Miguel Sousa Loureiro

Abstract

This dissertation of the Master degree in Chemical Engineering consists on the evaluation of the application of a 3D printer on mould creation for use in Soft Lithography PDMS-based device fabrication in separated parts, later joined with Chemical bonds to complete the chip intended for microfluidic applications.

Furthermore, this work describes the refined method and its evolution throughout the journey, followed by the results obtained by each iteration step and there individual review. Finishing with the presentation of the method's strength, shortcomings and suitable applications in fields such as prototyping, education and laboratory research.

Keywords: 3D printing; Soft Lithography; PDMS.

Resumo

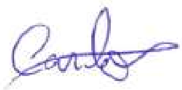
Esta dissertação do Mestrado em Engenharia Química consiste na avaliação da aplicação de uma impressora 3D na criação de moldes para utilização na fabricação, por Soft Lithography, de partes separadas de dispositivos baseados em PDMS, posteriormente unidas usando ligações químicas, mais especificamente usando ativação de plasma para quebrar as ligações químicas do PDMS na superfície e permitindo, por um curto período, a criação de novas ligações PDMS para PDMS entre as superfícies intendidas para junção, completando assim o chip destinado a aplicações microfluídicas.

Além disso, este trabalho descreve o método refinado e a sua evolução ao longo da jornada, seguido dos resultados obtidos em cada etapa da iteração e sua revisão individual. Finalizando, com a apresentação dos pontos fortes, pontos fracos e aplicações adequadas do método em áreas como prototipagem, educação e pesquisa laboratorial.

Palavras chave: Impressão 3D; Soft Lithography; PDMS.

Declaration

I hereby declare, under word of honour, that this work is original and that all non-original contributions are indicated and due reference is given to the author and source.



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Notation and Glossary

List of Acronyms

3D	Three Dimensional
CAD	Computer-Aided Design
CNC	Computer Numerical Control
DLP	Digital Light Processor
EDM	Eletrodischarge Machining
ECM	Eletrochemical Machining
FDM	Fused Deposition Modeling
FIB	Focused Ion Beam
G-code	Geometric Code
HD	High Definition
kB	Kilobyte
LCD	Liquid Crystal Display
MEMS	Microeletromechanical Systems
MSLA	Mask Stereolithography
PDMS	Polydimethylsiloxane
SLA	Stereolithography
SLS	Selective Laser Sintering
STL	Standard Triangle Language
UV	Ultraviolet

Chapter 1

Introduction

1.1 Motivation and Objectives

Currently, in the microfluidic chip manufacturing field, no method can provide complex 3D channels with low cost and rapid production time that research laboratories and educational institutions could apply. In this work, we aim to combine the advantages of 3D printing and Soft Lithography to address this gap.

The application of this work's results will benefit the fabrication of custom-designed microfluidic devices by greatly reducing the prototyping time and price and enabling more complex geometries inside the chips.

This theme came to be from the request I made to Dr. Francisco José Galindo Rosales for a thesis theme in his area of work since I enjoyed learning from his module in the class named "Materiais Poliméricos na Indústria" that focused on polymers. Taking in account my previous experience in CAD and in the operation of a FDM 3D printer, an evaluation of what would be possible and interesting for me to work on was done with the result of this dissertation's theme.

Though out this work, I learned and developed technical experiences in CAD, 3D printing with resin, microfluidicdevices, critical thinking in the compromises between technical/practical designs and problem solving.

At the beginning of the project there were defined the following main objectives:

- Design and print resin moulds;
- Select the most suitable resin to use with PDMS;
- Manufacture a system for aligning and assembling the chips;
- Produce, validate and characterize the quality of the chips produced;
- Prepare a user manual of the fabrication method;

1.2 Structure of the Dissertation

This thesis is organized into five chapters. Chapter 1 lays the groundwork for this study by establishing its motivating factors and outlining the objectives it seeks to achieve.

Chapter 2 provides a brief overview of the field of microfluidics field and examines the current state-of-the-art manufacturing methods.

In Chapter 3, there is a detailed description of each material and method recommended in this work.

Chapter 4 presents the main results of this study, accompanied by a detailed discussion of each.

The final conclusions are presented in Chapter 5 alongside the evaluation of the objectives, the environmental impact that this work can have, the mention of side projects and the final assessment.

Finally, the Appendix A provides with complementary technical information regarding the manufacturing processes.

Chapter 2

Context and state of the art

2.1 Introduction of Microfluidics

As we know it today, the field of Microfluidics was born from an expansion of Micro ElectroMechanical Systems in the 1990s. It can be defined as follows:

> "the science of manipulation of fluids in systems of micrometric size" [2].

The scale in question has a normal range of 100 nm to 1 mm for example in nature the tree's sap channels are visible in the leaves and the human body the blood flowing in the arteries, veins and capillaries [2]. This makes Microfluidics useful in areas such as separations, cell analysis, and microreactors [3].

To work in this field in the laboratory, we use devices called microfluidic chips (as shown in Figure 2.1) that are blocks of some chosen material with carefully engineered channels inside with micrometric scale. These devices are specifically made for a procedure with fast operation time, perfect for laboratory applications and research [4].

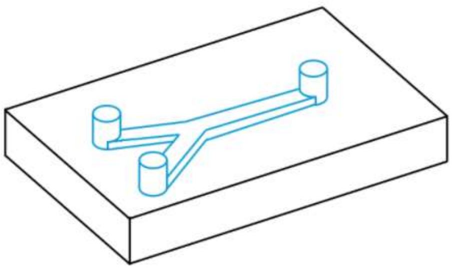


Figure 2.1: Drawing of a Microfluidic chip.

There are five main classes of materials for manufacturing microchips this are inorganic materials, elastomers and plastics, hydrogels, paper, hybrid, and composite materials. A well-thought-out analysis is crucial for choosing the most suitable material for the intended application, since research and commercial uses have different requirements and budgets [5].

Inorganic materials such as glass and silicon were the first-generation materials of this field [5] and have a great deal of desirable properties for instance, the glass' chemical resistance, optical transparency, thermal stability and the additional ease of cleaning [6].

The Elastomers and Plastics class can be further divided into elastomers, thermosets and thermoplastic [5]. When we talk about elastomers we are mainly talking about Polydimethylsiloxane (PDMS), which is the most used elastomer in the prototyping of microfluidic chips [7]. It is an interesting material for its proprieties of high chemical resistance, moderate durability, low cost, good minimum feature size, flexibility and biocompatibility etc. [3]. Thermosets plastics are known for their post-cure strong resistance and high costs, such as SU-8 and polyimide used in negative photoresists [5]. Furthermore, SLA 3D printing uses resins that are also categorized as thermosets, and these resins are associated with more affordable prices [8]. Thermoplastics such as polyurethane and polycarbonate are interesting for their high bond coverage, mechanical strength, optical clarity and durability [6].

Hydrogels are valued by chemists for their permeable structure since in aqueous mediums 99 % of the gel can be water [5], flexibility, biocompatibility and ability to be combined with conductive materials [6].

The paper class is the most basic and simple, also used by researchers [5].

Finally, the hybrid and composite materials class combines materials for example the combination of PDMS and glass [5].

2.2 State of the art

In the fabrication of microfluidic devices, there are a plethora of methods to choose from, and each has its place for a particular application. These methods can be divided into direct manufacturing and typical replication methods [1].

2.2.1 Direct Manufacturing

In these types of methods, the work is done on the final device by mechanical methods, energy-assisted methods or other alternatives.

Mechanical methods, normally subtractive, use tools or particles to remove material. Some examples are micromilling in a computer numerical control (CNC) using small spindle rotates at high speeds to micromill hard materials, this method is limited by the tool access and durability [9]; ultrasonic micromachining using abrasive particles and vibrations with a tool to cut, it works in smaller dimensions than the microcutting method, its cost-effective and can work with hard and brittle materials, but it wears the tools used in the process [10].

Energy-assisted methods can be subtractive or additive and use different sorts of concentrated energy [1]. For example, Eletrodischarge Machining (EDM) and Electrochemical Machining (ECM) use electrical potential to remove material [11] but this must be conductive [1], while Focused Ion Beam (FIB) uses ions to remove or add material with kinetic energy [12], it has high resolution and compatibility with all kinds of materials but it is slow, works in a small area and needs a vacuum environment [1], then the laser ablation uses the laser to remove materials such as metal, ceramic, glass and polymers [13] and micro stereolithography uses the laser to cure resin so its additive [14], and to finalize the electron beam machining uses electrons to slowly remove material inside a needed vacuum environment. These methods are used for greater precision applications and have a sizable machine cost [1].

Other alternatives include the Traditional Microelectromechanical Systems (MEMS) such as photolithography and wet/dry etching that were directly taken from the semiconductor industry [14], typically uses glass and silicon [9]; and 3D printing methods that in recent years have been increasing in interest [15] and are one of the bases of this work in the creation of a mould.

This type of manufacturing achieves the precision necessary but is not viable for volume production due to the time and cost spent on each device [1].

2.2.2 Replication Methods

These methods are based on fabricating a negative mould to make the microfluidic devices. The mould-making process uses some of the previously presented direct manufacturing methods. These types of methods can be further divided into Low and High volume production [1].

2.2.2.1 Low Volume Production

In this category, we have Soft Lithography, where normally PDMS is poured over a mould made from a positive photoresist such as AZ 40XT or from a negative photoresist such as SU-8 [7]. Typical manufacturing methods of SU-8 moulds require costly cleanroom environments [9]. It is also possible to produce 3D printed mould for soft lithography that replaces more time-consuming and costly methods [15]; Laminate manufacturing is based on the creation of individual layers later assembled on top of each other making the device, low cost but time-consuming [1]; Xurography that is a simple method for single layer devices and low cost and fabrication time suitable for educational and proof-of-concept objectives [3] and others such as laser fabrication.

Furthermore, these methods need a bonding process in order to prevent leaks; the main three types are chemical with UV/Ozone or plasma activation, thermal, raising the temperature to the glass transition, and adhesive with resins or curable materials. The bonding can be of the same or two distinct materials. Normally requiring flat and clean surfaces that increase the overall cost and complexity [7].

2.2.2.2 High Volume Production

In this category, we have processes like Hot embossing the mould is pressed to a polymer at high temperature and pressure demonstrated in side A of figure 2.2, Injection Moulding were a melted polymer is injected in the mould demonstrated in side B of the figure 2.2, Microthermoforming using thermoplastic films in the glass transition to stretch around the mould, ultimately these three methods are limited to use polymer materials, and others such as Film or Sheet Operations, Roller Embossing, and Roll-to-Roll (R2R) Processing for Flexible Electronics [1].

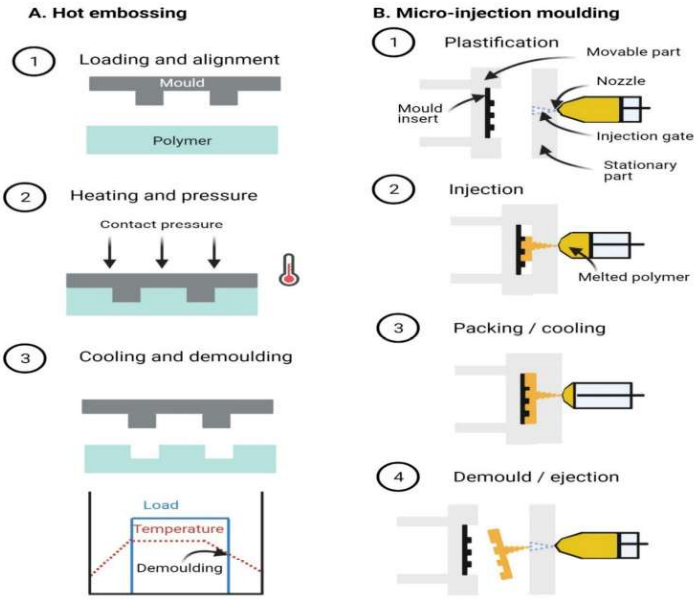


Figure 2.2: Schematic for (A) hot embossing and (B) micro-injection moulding. *Licensee MDPI, Basel, Switzerland. This article is an open-access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license, from* [1].

2.2.3 Summary of the State of the art

Currently, there are numerous methods to manufacture microfluidic devices. However none of them satisfy the conditions of low materials and machine cost, capable of complex 3D structures and with rapid fabrication time that are valuable for application in fields such as prototyping, education and laboratory research.

This work aims to fill this gap in the manufacturing methods by using a 3D printer to create resin moulds to be used in soft lithography, diminishing the negative side of cost time and geometric restrictions of mould manufacturing.

Chapter 3

Materials and Methods

3.1 3D Printing Process

3.1.1 Mask Stereolithography (MSLA)

In the 3D printing field, there are three main types of printers: Fused Deposition Modeling (FDM), Stereolithography (SLA) and Selective laser sintering (SLS). For this work, the most suitable type is SLA for its blend of resolution and cost as well as the fact that they use resins for the printing material.

This work used an Elegoo Mars 5 Ultra seen in Figure 3.1, which is an MSLA printer, a variation of SLA printers that uses a mono LCD as a mask to block the light in the regions of the design where the resin will not cure. This type of printer is more affordable and has exponentially faster printing times for larger volumes since each layer is exposed to light at the same time is not dependent on the laser's focal point and provides good resolution for the price.

Figure 3.1: The Elegoo Mars 5 Ultra.

3.1.2 Resins

As previously mentioned in Chapter 2.1 the resins used in SLA 3D printing are categorized as thermosets. This material was chosen for its durability, temperature resistance, and detail.

In this work there were used three types of resin shown in Figure 3.2:

- *The Everyone standard clear red* [16] that is going to be referred to as the red resin;
- *The Formfutura engineering series heavy duty grey* [17] that is going to be referred to as the grey resin;
- *The Smart materials 3D dental HD* [18] that is going to be referred as the dental resin;

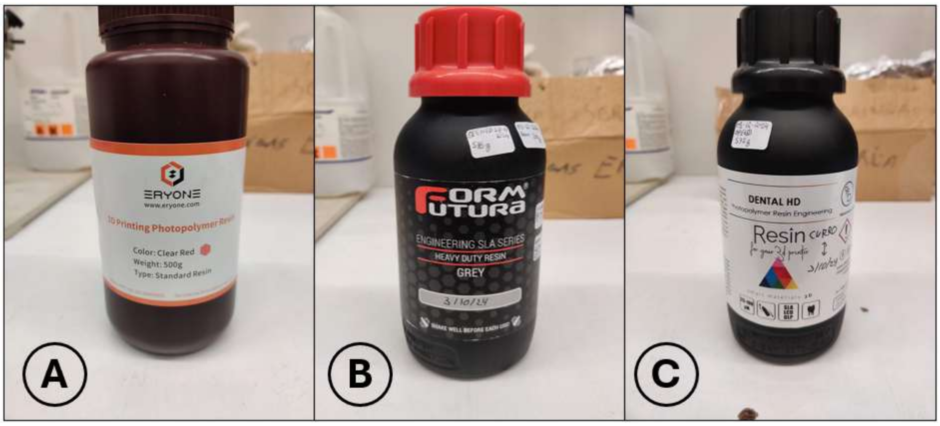


Figure 3.2: The Resins used. In A The Everyone standard clear red. In B, the Formfutura engineering series is heavy-duty grey. In C the Smart materials 3D dental HD.

3.1.3 Modeling

To start the process, it is recommended to make a list of the main objectives and characteristics the mould must have followed by a simplified sketch using a pencil and paper to help with the visualization process as seen in figure 3.3, keeping in mind that the dimensions have to be inside the resolution of the 3D printer. Simultaneously, evaluate the weak points that can result in partial or total failure in the following steps, such as printing, build plate release and curing process.

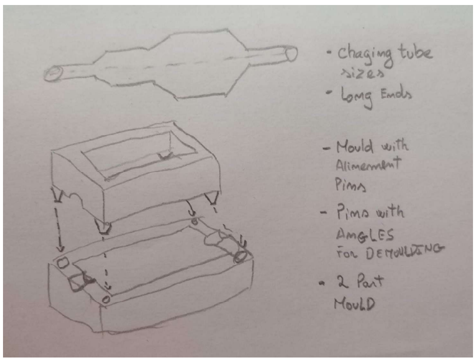
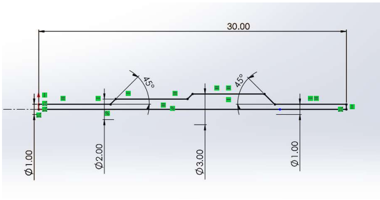
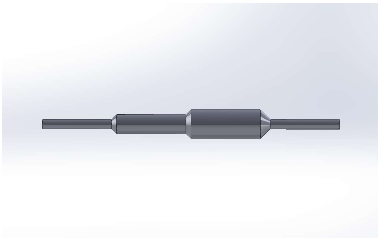


Figure 3.3: The paper list and sketch.

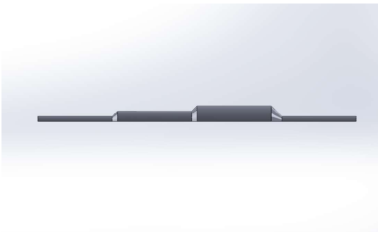
Once a general idea of the geometry and dimensions are established, proceed to a Computer-Aided Design(CAD) program. In this case, it was chosen Solidworks because of previous experience with the software inside the academic environment of FEUP. In summary, to design a 3D part, for example, the cylindrical variable size tube used in this work, start with sketching on one plane as shown in Figure 3.4a. Then extrude material; in this case, it is called a revolve since it is cylindrical, Shown in Figure 3.4b. It is also possible to use a sketch for the removal of material, as shown in Figure 3.4c. When all the mould parts are done, an assembly can be virtually made to check the rough fitment as shown in Figure 3.4d.



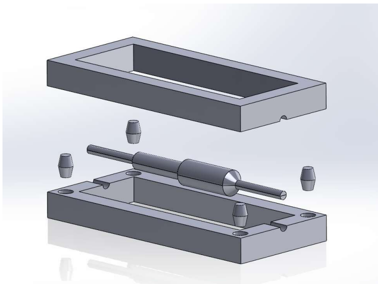
(a) sketch tube



(b) Complete tube



(c) Half tube



(d) Assembly visual check

Figure 3.4: Solidworks cylindrical variable size tube design

To end this step, these parts are exported in the Standard Triangle Language, better known as ".stl" file, typically with two-digit kB of size, which will be later used on the slicer.

3.1.4 Slicing

A FDM 3D printer works by taking in information read from a G-code file or geometric code [19] that contains layer by layer commands that tell the tool path, the speed and acceleration to move how much to extrude, what temperature and other parameters. For our MSLA printer, since it uses an LCD, the code must contain images to display the masks. In order to do so, the file must have an encoded compression, for example, the ".goo" files.

The slicer is the software in which the designed parts are divided into layers and joined by the printing parameters in a way that the printer can process.

The machine category that include information of the build area, volume of the machine, resolution and any offsets. Normally the software has a catalog of makes and models of 3D printers.

The printing category with the following main parameters:

- Layer height, which is associated with quality, since the lower the height of the layers, the less noticeable they are and the smoother the final print gets, but this lower height greatly increases the overall time of the printing process.
- Bottom layer count and exposure time will isolate a certain number of initial layers as the bottom ones and control their time in contact with the curing light separately from the rest of the layers. This is very important because the first layers of any print are critical for a successful print by setting a good contact with the build plate that the latter layers can build upon.
- Exposure time, is the time each layer has in contact with the curing light. On one hand, if this time is lower than needed, the resin will not cure completely, causing some design features to get less defined or even delamination of the layer. On the other hand, if this time is higher than needed, the resin will cure beyond the intended area, leading to less precise details and a more timely printing process.

In the slicer, it is important to create one profile for each resin because each has its printing parameters. The manufacturer's recommended printing parameters can be found in either the bottle or the company's online page; this information is a great starting point but doesn't allow lead to good results due to different environments such as temperature, humidity and so on.

In this work, it was necessary to perform various calibrations prints for the grey and dental resins going beyond the manufactured recommended printing parameters in order to get successful prints. The red resin worked well with the bottle's parameters, and even in conditions where the layer height was set at a lower amount than the 0.05 mm recommended, the results were satisfactory. The final printing parameters for the three resins are shown in Table 3.1.

Table 3.1: Resin's Printing parameters

Parameters	**Layer Height (mm)**	**Bottom Layer Count**	**Bottom Layer Exposure Time (s)**	**Exposure Time (s)**
Red	0.01	2	35	3.5
Grey	0.05	4	64	4.5
Dental	0.05	4	60	4.75

For this work, the chitubox software was chosen since it was compatible with the printer. Once the parameters were set, import the ".stl" files, choose their orientation, keeping in mind not to create cavities where the resin might be trapped during the printing process, and move the parts to the desirable location. It is recommended to keep the part away from the build plate in the z-axis for an easier release in post-printing. In this work, 10 mm was the standard, and insert supports were needed to connect the part to the building plate in a safe manner to avoid a structure collapse during printing, as shown in Figure 3.5. To end the slicing process, run the program and save the generated ".goo" file that contains encoded images, typically with five or six digits of kB of size.

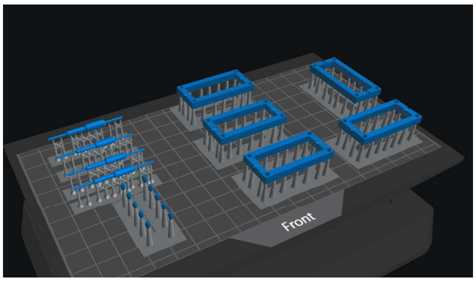


Figure 3.5: Build plate example of the slicer.

3.1.5 Printing

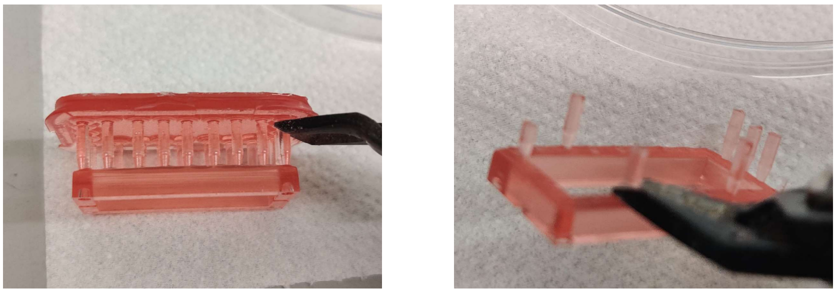
To begin the printing process, it is important to check the machine state is ready to print, the resin quantity is sufficient for the intended print and the resin's quality did not settle at the bottom of the tank as we can see in Figure 3.6, in this case, it is recommended to gently mix the resin with a plastic spatula being careful not to damage the resin release film at the bottom of the resin tank. Insert the ".goo" file and start the print. The printing time is related to the parameters, size, and orientation of the part; since the work is on a small scale, the approximate meantime would be around two hours.

Figure 3.6: Dental Resin settling particles.

3.1.6 Post-processing

At the end of the printing process, it is needed to remove the printed parts from the build plate by using the metal scraper. Some force may be needed in larger contact areas it is recommended to carefully tap the scrapper using it as a chisel to remove the part with supports attached or, alternatively, try to cut the supports first as a last measure since they can help to keep the part from warping latter in the curing process.

Once the parts are released, they need to be cleaned with alcohol, which was used 2-propanol in Appendix Figure A.2 inside a tank in Appendix Figure A.1a to remove unreacted resin. Then, the parts proceed to the curing machine that will complete the post-printing cure of the resin by using UV light and a set temperature, in this work, the Formlabs form cure shown in Appendix Figure A.1b, normally 90 min of UV at 65 ºC but these parameters can be adjusted depending on the part. Once, the cure is done the supports can be removed in two steps, by cutting first the base way from the surface of the part, as shown in Figure 3.7a and then at the surface of the part with care, as shown in Figure 3.7b, some further adjustments with sandpaper can be necessary and the final cleaning and stored in a labelled container.



(a) First cut (b) Second cut

Figure 3.7: Support removal.

3.2 Moulding Process

3.2.1 Materials

> "The PDMS is composed of a two-part heat-curable mixture. The pre-polymer is cross-linked with the curing agent usually in a 10:1 ratio in weight, but varying this ratio one can obtain different mechanical and chemical properties of the resulting mixture" [7].

To prepare the PDMS is measured in a cup the elastomer base and curing agent shown in Appendix Figures A.3a and A.3b respectfully, both from Sylgard 184, in a 9:1 weight ratio for a quicker curing time and greater strength, then with a spatula is mixed until a homogeneous solution is achieved and placed in a vacuum chamber in order to remove the bubbles, as shown in Figure 3.8.

Figure 3.8: Vacuum chamber.

3.2.2 The mould preparation

The mould preparation is one of the most crucial steps in this method because it is the last opportunity for small adjustments before the pour.

In a flat piece of glass laboratory its known flatness is important because the surface of the pour must be as flat as possible to ensure a better bonding process, place the resin moulds and check their flatness by tapping each corner, if the resin assembly tips that means there is a gap in the surface adjacent to the glass that will cause a spill in the pouring of the PDMS. In some applications, spilling can be acceptable since the elastomer has a big viscosity and, in the oven, it cures in less than an hour. In the other cases the resin assembles will have to go back to sanding or redesign, In the alternative the operator can place some weights on top, as shown in Figure 3.9 to force the gap to close as long as the weights don't contact the PDMS and this can affect the reuse of the mould since by forcing the resin in the oven it can warp the parts.

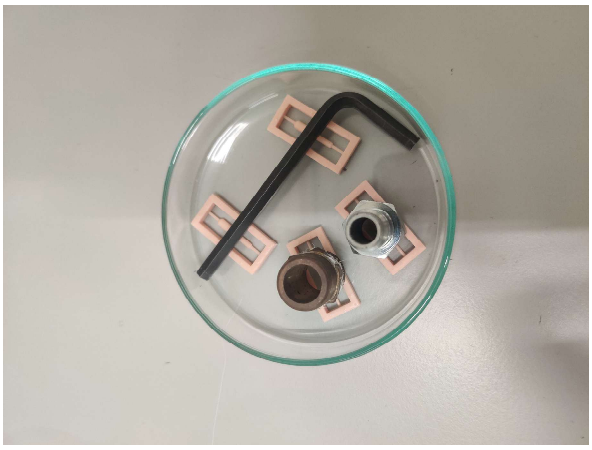


Figure 3.9: Weights on top of the mould.

3.2.3 The filling process

The pouring process can be done by directly pouring from the cup or by using a syringe with a large tip, as shown in Appendix Figure A.4 since the PDMS has a big viscosity. In this step, it is important to check for bubbles since, if there are any, they will be visible in the final product. Then, the parts go to the oven in Appendix Figure A.5 at 80º C for around an hour depending on the part and resin used.

3.2.4 The De-moulding

During the de-moulding process, cut out the spilt PDMS,as shown in Figure 3.10, then extract the whole chip and mould from the glass petri dish by angling the scalpel, as shown in Figure 3.11. If the extraction is done well, it should leave minimal residue on the glass surface in Appendix Figure A.6.

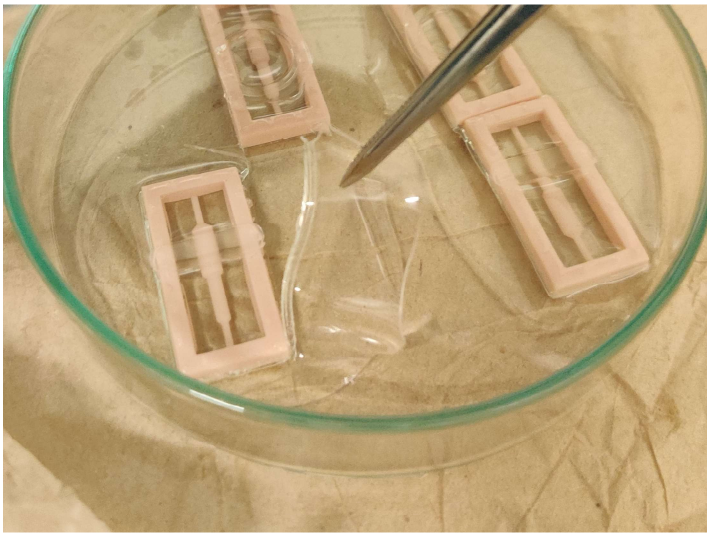


Figure 3.10: Removal of spilt PDMS

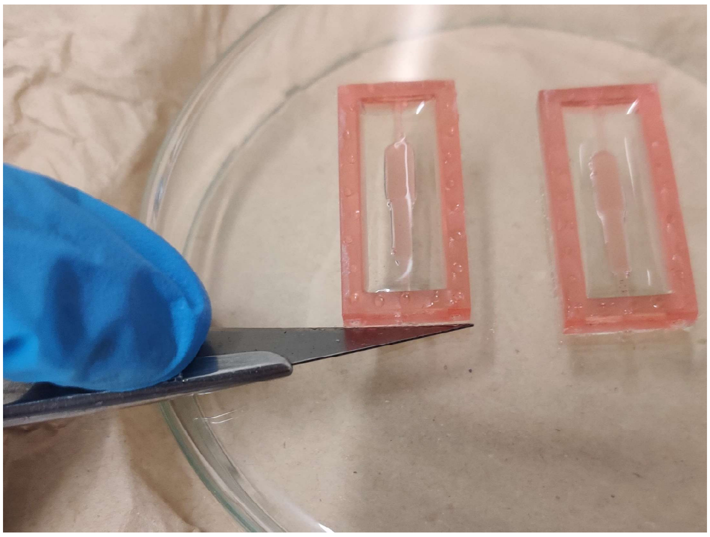


Figure 3.11: Scalpel angle of chip extraction.

3.2.5 The binding

In the final process, the microfluidic device's parts are bonded in this work, it was used a chemical approach, more specifically, by using plasma activation to break the chemical bonds at the surface of the PDMS and enable a short duration the creation of new PDMS to PDMS bonds between the intended bonding surfaces. This process is done in the Diener electronic Plasma-surface-technology ZEPTO machine present in Figure 3.12 with a stream of air instead of pure oxygen since air has a composition of 21% oxygen.

Figure 3.12: Diener electronic Plasma-surface-technology ZEPTO

The half chips are placed on a disc, as shown in Figure 3.13, and go inside the chamber with the intended merger surface facing up as shown in Appendix Figure A.7. The vacuum pump is turned on, and the chamber's lid is held by hand with a small rotation to help it seal correctly.

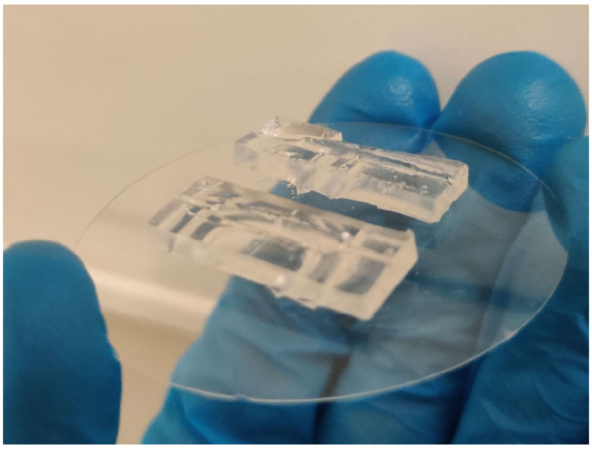


Figure 3.13: Half chips on the disc prepared for the biding process.

When the pressure is around 0.4 mBar, the first valve is slightly opened, making the pressure rise, while at around 0.9 mbar, the plasma generator is turned on for around 30 seconds. Then, the vacuum pump is turned off, and its done gentle ventilation is to atmospheric pressure; if the ventilation is too rapid, the parts inside the machine can move as shown in Appendix Figure A.8. The very last step is to carefully connect the two surfaces with the help of the mould in order to align them correctly completing the microfluidic chip manufacture.

Chapter 4

Results and discussion

4.1 The Sequence of Processes

The main result of this work is the final sequence of processes presented in the last chapter that enables the creation of a microfluid chip in a rapid, timely, and budget-friendly way.

4.1.1 Timeline

To emphasise the quickness of this sequence of processes, let us follow this timeline example based on my time spent in each process (Figure 4.1).

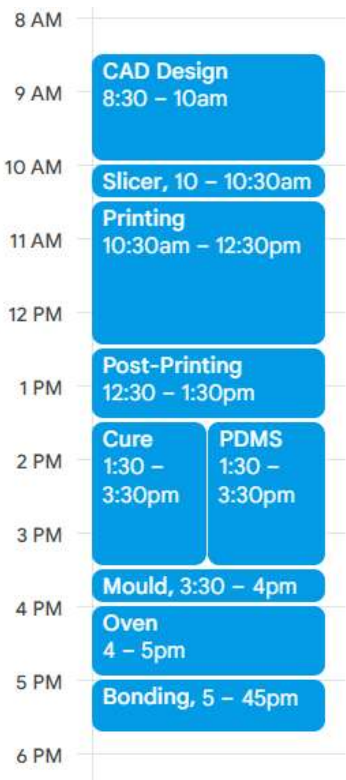


Figure 4.1: Timeline visual representation.

The process starts with developing an idea and its CAD design in around 90 minutes; then, run the .stl file through the slicer and begin the printing process in less than half an hour since the slicer should have the resin profiles already defined. The printing time takes around two hours, depending on the number of pieces and their size.

In the evening, the post-printing process will proceed for half an hour to clean the printed parts and, if necessary, remove the supports. Then, the curing process would take another 90 minutes, with some time for the machine to warm up to the starting 65 ºC; as the operator does not need to be present during the UV treatment, he can begin the preparation of the PDMS and warm the oven.

When the curing was done, it would take half an hour to prepare and fill the mould with PDMS. Finally, another hour in the oven for the PDMS crosslinking.

The final step of de-moulding and running the plasma machine will be done carefully and will take 45 minutes.

4.1.2 Cost

To emphasise the low cost of manufacturing equipment and materials, price tables are presented in Tables 4.1 and 4.2, respectively. As we can see, the total equipment cost was 10 695.49 €, making the plasma cleaner the most expensive one. This device was already available in CEFT's facilities; however, it would be possible to considerably reduce the equipment cost by purchasing an atmospheric plasma torch. The material's estimated price per chip would vary according to the resin chosen, costing between 2.59 and 3.10 € just in resin and PDMS. Other costs include electricity for the machines, alcohol used in the cleaning tanks and other standard laboratory instruments and equipment, such as glass and plastic-containing beakers, the oven, syringes, pliers, scalpels and tweezers.

Table 4.1: Equipment Price Table

Equipment	**Price (€)**	**reference**
Elegoo Mars 5 Ultra	337.99	[20]
Formlabs Form Cure	922.50	[21]
Diener electronic Plasma-surface-technology ZEPTO	9 435	Quotation from 2013
Total	10 695.49	—

Table 4.2: Materials Price Table

Material	**Price (€)**	**Volume**	**Cost per chip**	**reference**
Everyone standard clear red (500ml)	19.99	5 ml	0.20	[16]
Formfutura engineering series heavy duty grey (500ml)	71.48	5 ml	0.71	[17]
Smart materials 3D's dental hd (500ml)	27.06	5 ml	0.27	[18]
Sylgard 184 elastomer kit (1.1kg)	262.59	10 ml	2.39	[22]

4.2 Resin performance

4.2.1 Red Resin

The red resin was the cheapest and the most user-friendly resin used in this work. Even without the resin's calibration, the printed part's quality was surprisingly good. No failed prints from the resin parameters were chosen based on the information provided in the container. We even exceeded the recommended minimum layer height, and it worked surprisingly well. After having tested all the resins, at the end of this Master Thesis, we returned to this resin because it provided the best results in the printing process, making it the best choice for our objectives at the end of the works duration.

The major drawback of this resin is that it leaves an interface of uncured PDMS that is prone to creating bubbles during the oven phase, which affects the final quality of the chip as we can see in the Figure 4.5. This phenomena is already documented in [23] and they solved it by airbrushing protective ink before the moulding process. Despite knowing the possibility of the occurrence of this phenomena we had to be specific since in the last ten years the resins available in the market have been increasing in quantity, quality and made some innovations in its properties. In addition, the compositions of the resins are not advertised due to the research and development work that the companies spend.

4.2.2 Grey Resin

The grey resin was chosen as the second option due to its heavy-duty designation, as evidenced by the additives visible during the resin's mixing process. According to the specifications, this resin was suitable for high temperatures and high pressures, which were interesting properties consideringthat at the time a possible higher temperature injection process of the PDMS was thinked about due to the faster PDMS cure time and the chip fabrication being one part that would need to be cutted to remove the resin inside mould rather then being two separate parts. However, this resing resulted into an unexpected amount of failed prints even after multiple calibrations. It was quite common to end up with only some of the parts sent to print on the building plate at random locations (one day it was only the back line, the next day the right). This inconsistency was a sizable speed bump in the work progress. However, we managed to print some parts by setting printing parameters defined outside the manufacturer's recommended range and discovered by trial and error attempts. In this way, it was possible to use this grey resin in the calibration of the PDMS time inside the oven with a cup-like design.

In parallel, the red resin parts were used in the PDSM moulding process to get to know the challenges and the results were acceptable despite the previously mentioned uncured PDMS phenomena, so we reconsidered the use of this grey resin and decided it was too inconsistent to continue with it in this study and not really needed for its properties.

4.2.3 Dental Resin

The dental resin was the third used for its precision, considering the PDMS moulding process and the better the mould part, the higher quality the final chip gets.

This resin did not have the uncured PDMS phenomena present in the red resin, but unfortunately, it gave us the same kind of printing problems as the grey resin in the unconsistency and dificulty of the printing process.

An additional observation is that this dental resin had the additives settled at the bottom, visible to the naked eye, as shown in Figure 3.6 in the appendix.

4.3 Assessment of the printed parts

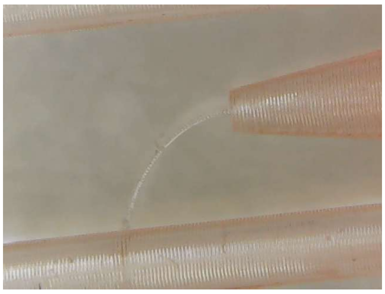
In the printing process, it was manufactured various designs such as complete and half tubes of various sizes printed in vertical and horizontal orientations, some different shapes of tubes, the assembly of the tube mould used in the chip's manufacture successfully, and other parts that do not represent the printing results in the design aspect such as calibration of the printer parts, PDMS calibration cup-like parts or other works parts.

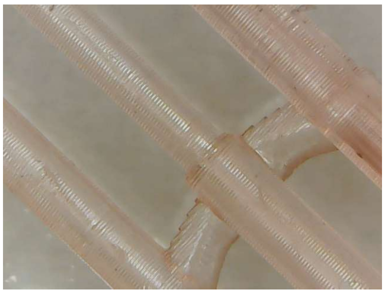
4.3.1 Effect of gravity on the printed parts

In the vertical orientation, the number of layers was greater than the horizontal orientation, which correlated to a greater print time. The results were unsatisfactory since there was a greater amount of warping, stretching and breaking, shown in Figures 4.2a 4.2c 4.2d respectively, due to the force of release from the tank's film being applied perpendicular to the layer line, as seen in Figure 4.2b, making the part weaker in the most important direction in the printing process.

In the orientation perpendicular to the direction of gravity, there is the additional question of rotation of the part with the supports on the inside or the outside of the half-tube. The results showed that where there was a support, the part warped or slightly chipped in removing said support, as we can see in the Figure 4.3.

The best results for this work's intended application were the horizontal orientation with the supports on the inside of the half tube since that surface will be sanded and is not in contact with the PDMS during the chip's manufacture.


(a) Warping


(b) Detailed layer lines


(c) Stretching of layers

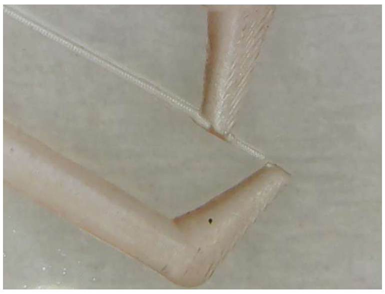
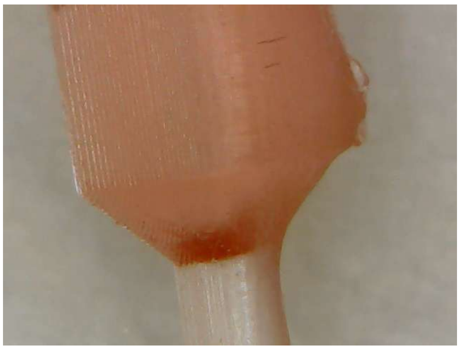
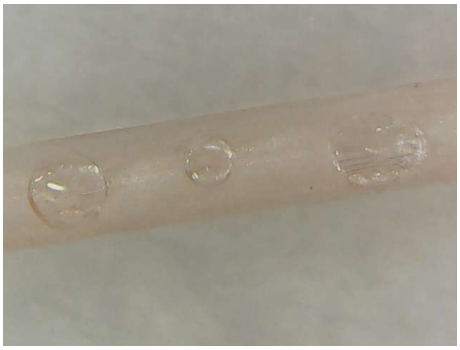
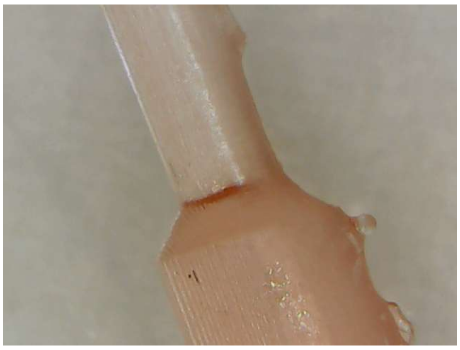

(d) Breaking between supports

Figure 4.2: Results of the printed parts with its major dimension aligned with the gravity. *Images taken with a Unotec USB digital microscope.*


(a) Outside shape deformation


(b) Inside shape deformation


(c) No deformation between supports


(d) Detailed layer lines

Figure 4.3: Results of the printed parts with its orientation perpendicular to the direction of gravity. *Images taken with a Unotec USB digital microscope.*

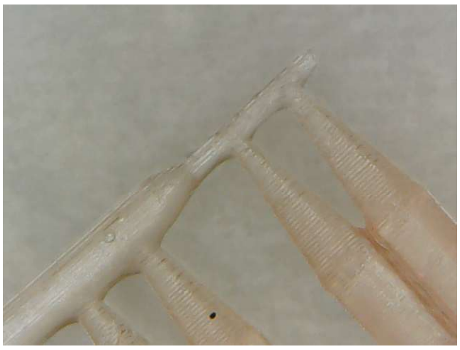
4.3.2 The Tube Shapes

As a test of the capabilities of the printer, there was a design of four-point star and rectangular-shaped tubes that transited from a typical cylindrical tube with 1.0, 0.5 and 0.25 mm of diameter in the tube, the 1.0 mm design shown in Figure 4.4c and 4.4f.

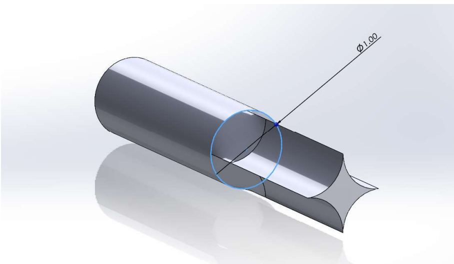
In the 1 mm dimensions, the results show a recognizable star shape and rectangle, as shown in Figure 4.4a and Figure 4.4d. In the other 0.5 mm the detail is reduced in both the start and rectangle, as shown in Figure 4.4b and Figure 4.4e.

For the dimensions chosen the results were promising and successfully showed the capability of the printer for more complex geometries.

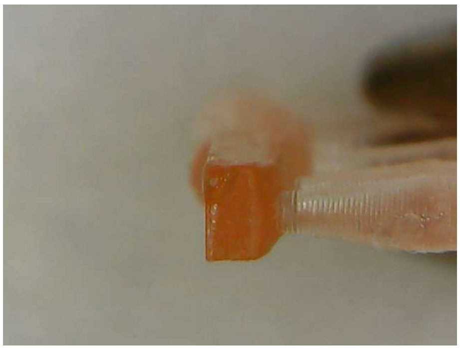
(a) Cross view of the 1.0 mm star print



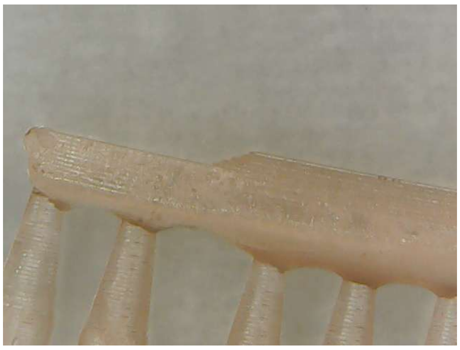
(b) Side view of the 0.5 mm star print



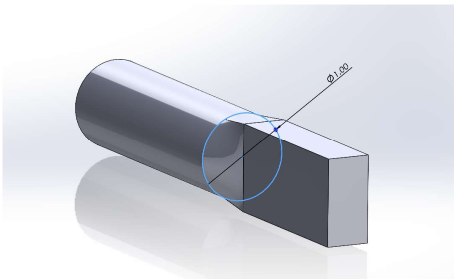
(c) CAD view of the 1.0 mm star print



(d) Cross view of the 1.0 mm rectangular print



(e) side view of the 0.5 mm rectangular print



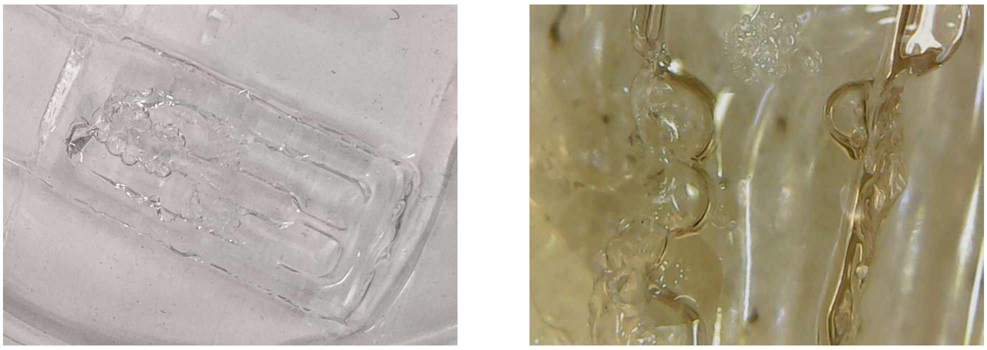
(f) CAD view of the 1.0 mm rectangular print

Figure 4.4: Results of the tube shapes print.
Images taken with a Unotec USB digital microscope.

4.4 Chip Results

4.4.1 Red resin chips

The first PDMS chips were obtained using the printed parts obtained with red resin. In this first attempt, no calibration of the oven time was performed. It was considered the typical curing time of half an hour used in softlithograpy with SU-8 moulds. As it can be observed in Figure 4.5, bubbles were formed in the uncured PDMS interface between the mould and the cured PDMS,as mentioned previously in chapter 4.2.1.



(a) Normal view of the pour

(b) Micro view of the bubbles. *Image taken with a Unotec USB digital microscope.*

Figure 4.5: Results of first PDMS Pour.

After some iteration, we discovered that one hour would reduce the amount of uncured PDMS, consequently reducing the number of bubbles and forming a chip with better quality, as shown in Figure 4.6.

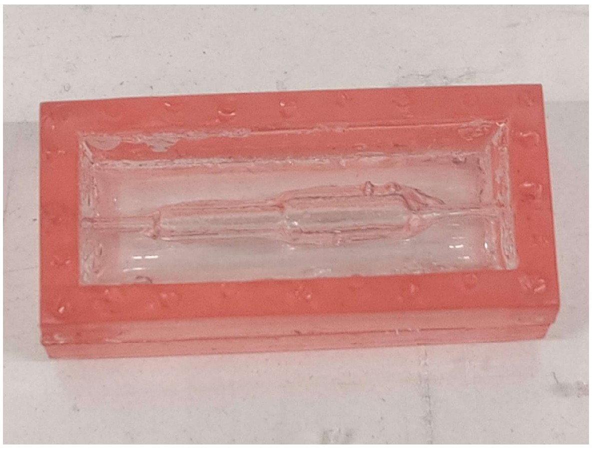
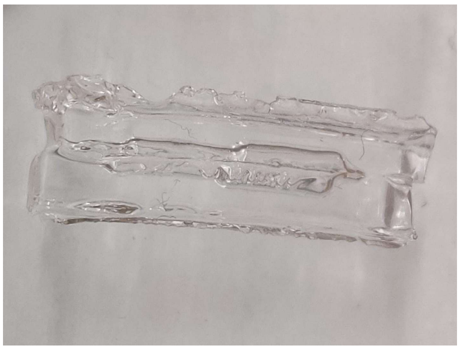


Figure 4.6: Results of red resin mould with one hour oven time.

The last chip done with the red resin mould was bonded by hand without the mould to align the surfaces as an experiment. We can see in the pictures 4.7 that it bonded very well, but with a slit unalignment; on one side, the tube was bonded shut.

(a) top view of the chip



(b) side view of the chip

Figure 4.7: Hand bonded chip

4.4.2 Dental resin chips

In this half chips removed from the dental resin mould, we can see the imprint of the weights used to press down the mould in the pouring phase due to an overfill of PDMS, as shown in Figure 4.8. Furthermore,as seen in Figures 4.9, the surfaces in this chip did not have clean results because the glass container used had walls that restrained the movement of the scalpel during the de-moulding process, but the insides had great quality. From this point forward, the glass container was turned upside down A.9 and gave better surfaces results.

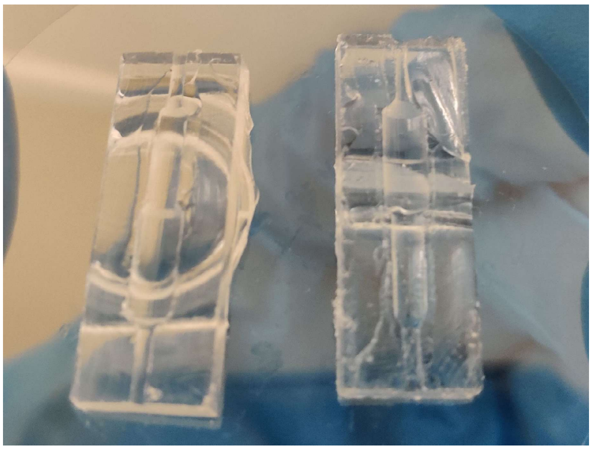
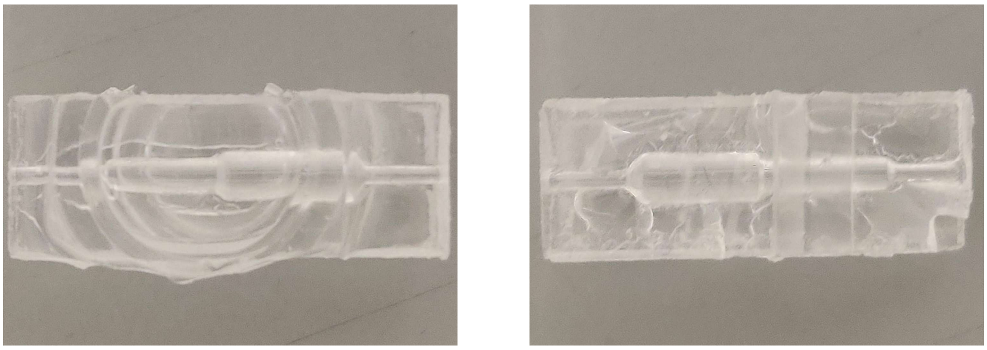


Figure 4.8: Results of dental resin mould with indentations and rough de-moulding.

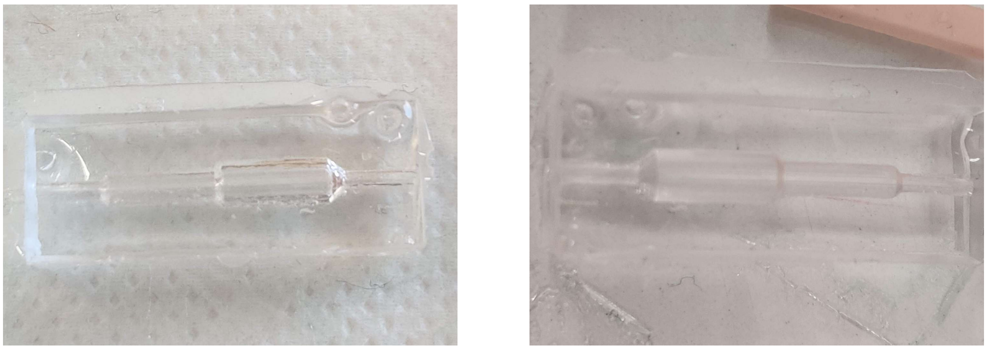


(a) top view of the chip with an circular imprint

(b) top view of the chip with an strait imprint and ruff surfaces

Figure 4.9: Imprinted chips

In the last chips manufactured with the dental resin, the moulds were scrapped and cleaned with ethanol and reused, this time using the supports as a bridge from the mould to the weights to avoid the imprint visible in the previous chip, as shown in Figure A.10. The addition of the supports made the transfer to the oven more challenging having to balance the assembly of mould plus the supports and weights, resulting in one of the supports moving and touching the PDMS, but the imprint on the chip was in a not important area, as seen in Figure 4.10a . This batch of chips had the best results in the quality of channels and surfaces, shown in Figures 4.10.



(a) The chip with the support indent on the top right corner.

(b) The quality of the chip.

Figure 4.10: The best quality channels and surfaces.

Chapter 5

Conclusions

This method is the sum of the 3D printing technology for mould creation, the Soft Lithography method for the device manufacture and its final step the Oxygen Plasma treatment that bonds the parts of the device.

With this merge of techniques, the final method has a rapid manufacture timeline, low cost manufacture, compatibility with 3D complex channels, good channel smoothness and moderate device durability due to the PDMS properties.

On the other side it has its disadvantages with the multiple manufacturing processes, low volume production, questionable mould durability, timely calibration phase for each resin chosen to print in this dimensions and finally its ultimately limited by the printer's resolution and the resin's minimum printing dimensions.

In sum, this method is a feasible solution for applications that treasure time and cost over the extended precision of other methods, such areas include prototyping, education and laboratory research.

5.1 Objectives achieved

Looking back at the main objectives of this work, the design and printing of a resin mould were done together with the manufacture of a system for aligning and assembling the chips. The resin selection is dependent on the application because the best result with the PDMS was expected to be the dental resin, but it had difficulties printing without failures. Thus, the best printing was the red resin, but it lacked in quality with the PDMS due to the interphase of uncured PDMS. The chips produced were seen in Chapter 4 with visually satisfactory results, and, at last, the manual of the fabrication method is detailed in Chapter 3.

5.2 Future work

Future work should focus on reducing the phenomena of the interface of uncured PDMS present in the results of the red resin (Section 4.2.1) with coatings in the mould preparation phase, on improving the printing process for the dental resin in order to produce more consistent results (Section 4.2.3) and design and test more complex 3D geometries since its one of the strong points in this method.

5.3 Impact in the Sustainable Development Goals

It's important to think about the impact that this work can one day have on the United Nations Sustainable Development Goals,and this work's contribution is presented in Table 5.1 below.

Table 5.1: Sustainable Development Goals

SDO	**Goals**	**Contribution**	**Performance indicators and metrics**
9	9.5	This works manufacturing process will provide inexpensive and simplicity to the microfluidic field research in all countries, in particular developing countries.	9.5.1 - Research and development expenditure as a proportion of GDP

5.4 Other works

During the duration of this work, some side projects were done, such as laboratory organization, running the slicing program with other work's files and printing them and a large amount of time spent on resin and PDMS calibration that did not directly participate in the fabrication of chips.

5.5 Final Apreciation

This dissertation was focused on practical work done in one semester, by my own choices and hands, with guidance from Dr. Francisco José Galindo Rosales during our weekly meetings. It was a valuable experience with good results, and knowledge learned differently from the theoretical or laboratory classes and the perfect end for this master's degree in Chemical Engineering.

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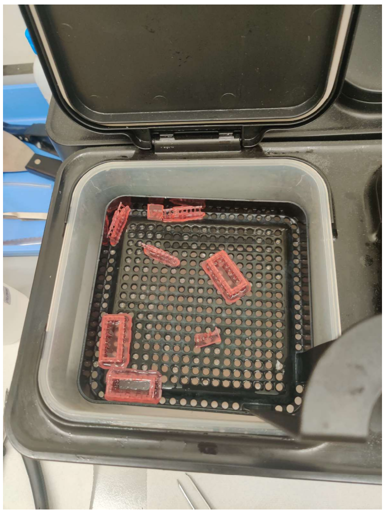
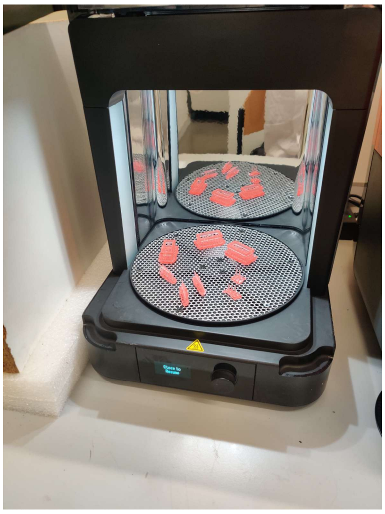
Appendix A

Additional information on the manufacturing process

Post-processing cleaning tank and the model Form Cure machine from Formlabs. Mentioned in chapter 3.1.6.



(a) the cleaning tank with propanol



(b) UV treatment in the Formlabs Form Cure machine.

Figure A.1: Post-Processing equipment.

This was the 2-propanol used in the cleaning steps of the resin. Mentioned in chapter 3.1.6.

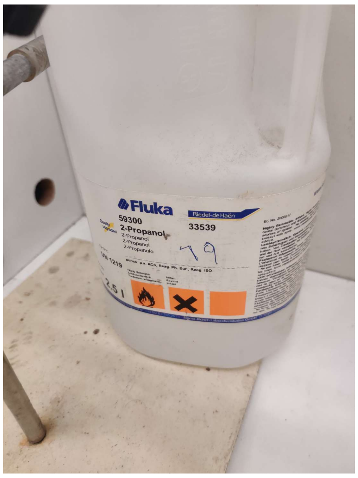


Figure A.2: Propanol container.

This was the PDMS elastomer base and curing agent mentioned in chapter 3.2.1.

(a) Elastomer base

(b) Curing agent

Figure A.3: PDMS components.

This was the syringe used in the pouring process. Mentioned in chapter 3.2.3.

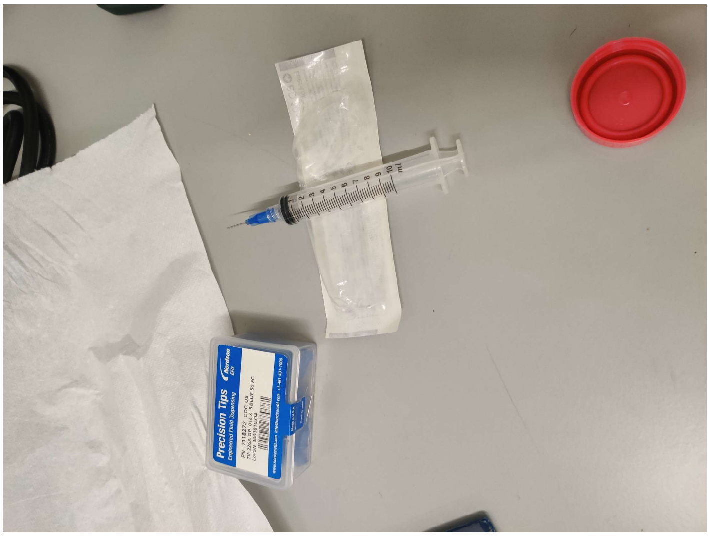


Figure A.4: Syringe and needle.

The oven, Model ED 23 from Binder, was used in the curing process. Mentioned in chapter 3.2.3.

Figure A.5: Model ED 23 from Binder.

Here we have the residue left from the chip extraction in the de-moulding process. Mentioned in chapter 3.2.4.

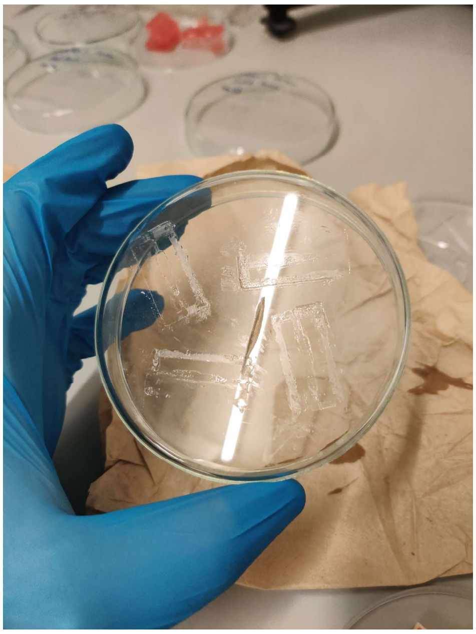


Figure A.6: Residue left from the extraction

The insertion of the parts in the Diener electronic Plasma-surface-technology ZEPTO machine for the binging process. Mentioned in chapter 3.2.5.

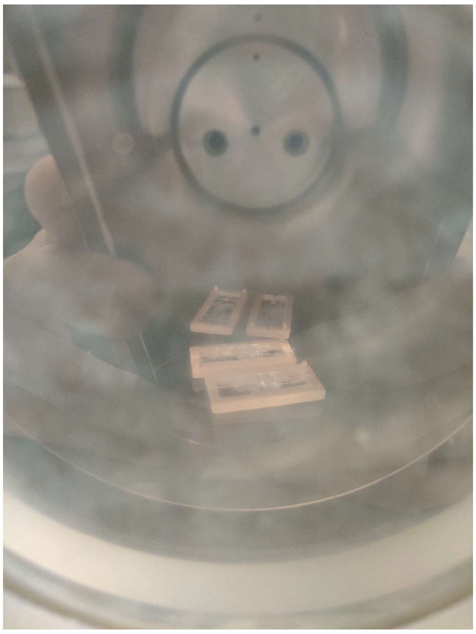


Figure A.7: Correct orientation of the parts in the Diener electronic Plasma-surface-technology ZEPTO machine.

The unexpected result is when the ventilation valve is opened too fast. The air pressure moved the parts inside. Mentioned in chapter 3.2.5.

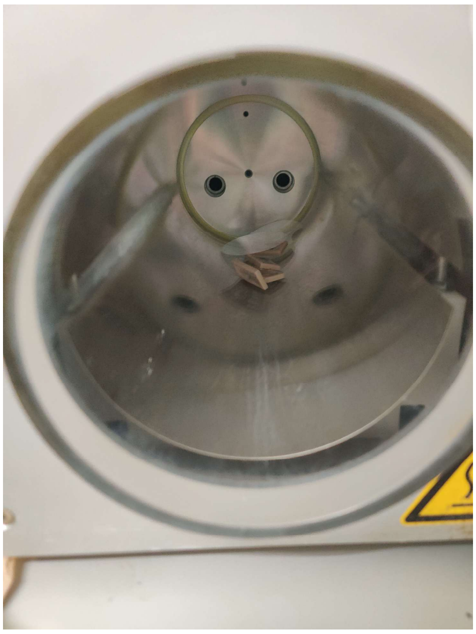


Figure A.8: result of a fast ventilation step in the Diener electronic Plasma-surface-technology ZEPTO machine.

A visual demonstration of the up side down container's surface used in chapter 4.4.2.

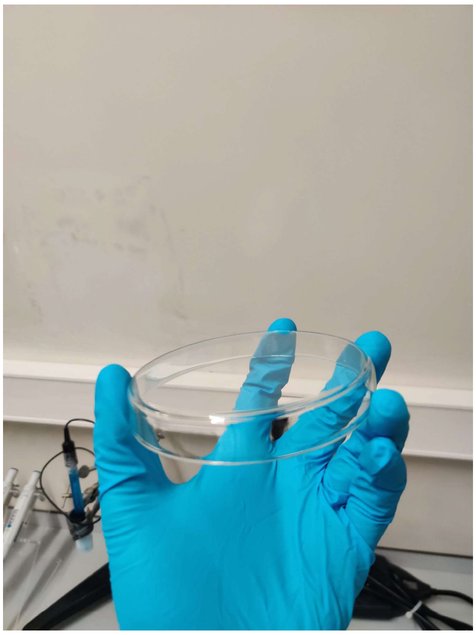


Figure A.9: Upside down glass container

A visual demonstration of the mould preparation setup is mentioned in chapter 4.4.2.

Figure A.10: Mould setup with support material between weights and mould.