

FACULDADE DE ENGENHARIA DA UNIVERSIDADE DO PORTO

Analysis of the extrusion flow in a Fused Deposition Modelling 3D printing process

Rui Filipe Barbosa Mendes



Master in Mechanical Engineering

Supervisor: Francisco José Galindo-Rosales

Co-Supervisor: Laura Campo-Deaño

Co-Supervisor at Ultimaker: Paola Fanzio

July 25, 2019

Analysis of the extrusion flow in a Fused Deposition Modelling 3D printing process

Rui Filipe Barbosa Mendes

Master in Mechanical Engineering

July 25, 2019

*“Tell me and I forget. Teach me and I remember.
Involve me and I learn”*

Benjamin Franklin

Resumo

Fabrico Aditivo tem o potencial para revolucionar toda a indústria tradicional de fabrico de peças e produtos. Uma das tecnologias de fabrico aditivo mais usadas é a deposição por extrusão, nomeadamente a Fused Deposition Modelling (FDM). Neste processo, um material termoplástico é alimentado para um liquidificador onde este é fundido e extrudido através de um bocal. O movimento da cabeça da impressora permite a deposição de material em locais específicos, camada por camada, construindo assim formas geométricas tridimensionais [1]. No entanto, a FDM é uma tecnologia relativamente recente, o que faz com que não exista um conhecimento profundo de todas as etapas do processo. Uma das etapas mais importantes de todo o processo é o controlo da extrusão, que pode ser afetado pela presença de um refluxo [2]. Neste trabalho, foi desenvolvido uma série de protótipos de canais 2D de microfluidica em PDMS replicando o bocal da impressora 3D, de forma a estudar o escoamento do fluido dentro dos canais. O principal foco deste trabalho passa por investigar a presença do já mencionado refluxo, possivelmente originado pela presença de vórtices a montante da contração devido à elasticidade do fluido de trabalho [3]. Para tal, foram recolhidas as propriedades reológicas de um policarbonato em escoamento de corte, à sua típica temperatura de impressão, recorrendo a informação disponível na literatura [4]. Uma vez que não é viável fazer escoar um fluido a estas temperaturas dentro dos canais de PDMS, para o trabalho de análise do escoamento, foram preparados dois fluidos viscoelásticos, que à temperatura ambiente pudessem replicar as condições de escoamento em termos de número de Reynolds e de número de Deborah. Foram ainda conduzidas experiências de visualização num microscópio óptico invertido, onde as linhas de corrente do escoamento destes fluidos análogos foram fotografadas através dos microcanais 2D. Finalmente, foi construído um mapa De-Re onde se consegue demonstrar que o escoamento tipo "backflow" pode ter origem nas recirculações observadas à montante da contração por causa das propriedades elásticas do fluido de trabalho.

Palavras-chave: Impressão 3D, reologia, escoamento viscoelástico, microfluidica, escoamento através de uma contração.

Referências:

- [1] N. Turner, B., Strong, R., A. Gold, S. (2014). A review of melt extrusion additive manufacturing processes: I. Process design and modelling. *Rapid Prototyping Journal*, 20(3), 192-204.
- [2] Gilmer, E. L., Miller, D., Chatham, C. A., Zawaski, C., Fallon, J. J., Pekkanen, A., Bortner, M. J. (2018). Model analysis of feedstock behaviour in fused filament fabrication: Enabling rapid materials screening. *Polymer*, 152, 51-61
- [3] Campo-Deaño, L., Galindo-Rosales, F.J., Pinho, F.T., Alves, M.M. and Oliveira, M.S.N. Flow of low viscosity Boger fluids through a microfluidic hyperbolic contraction. (2011) *Journal of Non-Newtonian Fluid Mechanics*, 166, 1286-1296.
- [4] John T Bendler. Handbook of Polycarbonate science and technology, CRC press, 1999

Abstract

Additive manufacturing (AM) has the potential to revolutionize the entire manufacturing industry. One of the most widely used AM technologies is extrusion deposition, such as Fused Deposition Modelling (FDM). In this process a thermoplastic filament is fed into a liquefier where is melted and pushed through a nozzle. The movement of the print head allows depositing the material in specific locations, layer-by-layer, building custom 3D geometries [1]. However, FDM is a relative young technology therefore, there is no in-depth knowledge of all stages of the printing process. One important stage is the control of the extrusion flow, which could be affected by the presence of a back-flow [2]. In this work we developed a 2D microfluidic device made of PDMS mimicking a simplified model of a 3D printing nozzle, to study the complex fluid-flow behaviour inside it. Our principal focus was to investigate the presence of the mentioned backflow inside the nozzle originated likely due to the presence of vortices upstream of the nozzle contraction as a consequence of the elasticity of the working fluid [3]. To do so the rheological properties of the characteristic polycarbonate under simple shear were taken from a handbook [4] at its typical printing temperature. Since it is not viable to work at these values of temperature and viscosity in a PDMS microfluidic device, two viscoelastic fluids were developed so that it was possible to replicate the real flow conditions of the polymer melt, in terms of Reynolds and Deborah numbers. Flow visualization experiments were also carried out in a inverted microscope where the streamlines of the fluids were photographed. Finally a De-Re flow map was built, where the upstream vortices associated to the backflow effect were presented.

Keywords: 3D printing, rheology, viscoelastic flow, microfluidics, contraction flow

References:

- [1] N. Turner, B., Strong, R., A. Gold, S. (2014). A review of melt extrusion additive manufacturing processes: I. Process design and modelling. *Rapid Prototyping Journal*, 20(3), 192-204.
- [2] Gilmer, E. L., Miller, D., Chatham, C. A., Zawaski, C., Fallon, J. J., Pekkanen, A., Bortner, M. J. (2018). Model analysis of feedstock behaviour in fused filament fabrication: Enabling rapid materials screening. *Polymer*, 152, 51-61
- [3] Campo-Deaño, L., Galindo-Rosales, F.J., Pinho, F.T., Alves, M.M. and Oliveira, M.S.N. Flow of low viscosity Boger fluids through a microfluidic hyperbolic contraction. (2011) *Journal of Non-Newtonian Fluid Mechanics*, 166, 1286-1296.
- [4] John T Bendler. *Handbook of Polycarbonate science and technology*, CRC press, 1999

Agradecimentos

Concluído este trabalho gostaria de manifestar os meus profundos agradecimentos aos que contribuíram para a sua realização.

Em primeiro lugar o meu mais sincero e profundo obrigado aos meus orientadores: o Doutor Francisco J. Galindo-Rosales e a professora Laura Campo-Deaño que mais do que orientadores foram mentores, porque não só me guiaram nas diversas etapas desta dissertação como também me transmitiram conhecimento em cada uma delas, de uma forma clara, com muito conhecimento do que estavam a transmitir, mas sempre de uma forma calma e relaxada, o que me deu confiança ao longo de todo o processo. Tiveram a disponibilidade e dedicação que qualquer estudante ambiciona quando entra neste processo, seja para tirar uma dúvida minimalista, seja nos vários treinos experimentais, seja a reorganizar a estrutura desta dissertação a que hora fosse. Se fiquei com gosto por este trabalho devo-o também a vocês e estou seguro que com outros orientadores este resultado não seria possível.

Uma palavra em especial para a minha família, em particular para os meus pais e irmã que estiveram ao meu lado não só este semestre mas também ao longo de todo o meu percurso académico. Festejaram as minhas vitórias, apoiaram-me nos meus obstáculos, não me deixaram desistir nas minhas derrotas. Estiveram lá sempre e foram essenciais na transmissão de valores e carácter que me fizeram chegar a este momento. Obrigado.

Aos amigos que me acompanharam durante estes 5 anos e que levarei para a vida pois percorreram este caminho comigo e que sem a sua ajuda dentro e fora da faculdade teria sido incrivelmente difícil. Aos amigos que já me acompanham há mais tempo, fora do contexto faculdade, que permitiram descarregar as frustrações e proporcionar alegrias ao longo deste percurso.

Agradeço à Ultimaker pela oportunidade que me deu em realizar este trabalho, transmitindo confiança num resultado positivo e que pudesse ser útil para o seu protótipo. Agradeço ao Centro de Estudos de Fenómenos de Transporte (CEFT) e a toda a sua equipa, em particular ao Tomás Pinto por toda a sua ajuda e disponibilidade demonstrada durante todo o processo de aprendizagem e no manuseamento do equipamento do laboratório e ainda ao Centro de Materiais da Universidade do Porto (CEMUP), em particular à Dra. Ana Queirós e ao Dr. Rui Rocha, por todo o auxílio na construção e visualização dos canais.

Rui Mendes

Contents

Abbreviations	xv
1 Introduction	1
1.1 Motivation	1
1.2 Objectives and structure	2
2 State of the art	5
2.1 Additive Manufacturing	5
2.2 Fused Deposition Modelling	6
2.3 Rheology	7
2.3.1 Viscoelastic Fluids	8
2.4 Contraction Flows	10
2.5 Microfluidics	12
2.5.1 Micro-device Fabrication	13
3 Materials and Methods	15
3.1 Rheological characterization of the polymeric material for 3D printing	15
3.2 Analogue fluid	16
3.2.1 Samples preparation	16
3.3 Rheometry Experiments	17
3.3.1 Start-up and Viscosity curves	20
3.3.2 Small Amplitude Oscillatory Shear (SAOS) tests	20
3.3.3 Extensional Rheometry	24
3.3.4 Errors and limits of reliability on shear rheometry	25
3.4 Microfluidics	27
3.4.1 Micro-channel design	27
3.4.2 Micro-channel fabrication	29
3.4.3 Flow Visualization	37
3.5 Dimensionless Numbers	40
3.6 Uncertainty analysis	43
4 Results and Discussion	45
4.1 Polycarbonate	45
4.2 Analogue fluids	48
5 Remarks and FurtherWork	65
References	67

List of Figures

1.1	Sketch of the annular backflow problem	2
2.1	Key components in FDM 3D printing	6
2.2	Viscosity as function of shear rate	8
2.3	Schematic streamwise view of an abrupt contraction flow	11
2.4	Entrance flow pattern in three different melts	12
2.5	Process for creating PDMS microfluidic channels	14
3.1	Mixing process of the analogue fluid samples	17
3.2	Anton Paar, model Physica MCR301 rheometer	17
3.3	Star-up Curve for 10000ppm PAA+water and 50ppm PAA+water with 70% Glycerol	20
3.4	Relation between storage, loss modules and complex shear modulus	21
3.5	Amplitude sweep at a fixed frequency used to determine the linear viscoelastic region	22
3.6	Storage and loss modules in a frequency sweep test	23
3.7	Haake CaBER 1, Thermo Scientific	24
3.8	Filament thinning process recorded with a high speed camera at 1000 fps	25
3.9	Filling of a plate plate geometry where: a) overfilled, b) underfilled and c) is the correct amount	26
3.10	Critical dimensions of the 3D printer nozzle	28
3.11	Micro-channel design with different scales	29
3.12	3D sketch of a micro-channel	29
3.13	Direct writting equipment	30
3.14	Pattern Mask fabricated with a AZ1505 photoresist	31
3.15	SU-8 mold soft baked onto a hotplate	32
3.16	Mask aligner exposing UV light onto the SU-8	32
3.17	SU-8 master molds	33
3.18	Silanization process	34
3.19	Cutting the PDMS from the SU-8 master mask	34
3.20	PDMS micro-channels at the end of fabrication	35
3.21	Scanning Electron Microscopy images of three types of micro-channels fabricated from high quality SU-8 photoresist moulds: a) Top view of 2D nozzle; b) View of the cross section of the micro-channel; c) Perspective image	36
3.22	Connecting the inlet and outlet ports in PDMS with a precision tip	37
3.23	Surface treatment of PDMS in a plasma cleaner	38
3.24	Fluorescent particles stuck at PDMS, creating very bright spots	38
3.25	Assembly and placement of the micro-channels for flow visualizations	39
3.26	Mercury fluorescent lightning	39

3.27	PDMS debris and air bubbles trapped inside micro-channels	40
4.1	Master curve of dynamic properties of PC54: reference temperature of 275°C . .	45
4.2	Viscosity curves for type A samples	48
4.3	Viscosity curves for type B and type C samples	48
4.4	G' G'' curves of 50,100 and 200 ppm PAA samples	49
4.5	De-Re flow map	53
4.6	Flow pattern for a Newtonian fluid at different flow rates. The flow direction is from left to right	55
4.7	Flow pattern for El=375 at different conditions. The flow direction is from left to right	56
4.8	Flow pattern for El=750 at different conditions. The flow direction is from left to right	57
4.9	Flow pattern for El=1500 at different conditions. The flow direction is from left to right	58
4.10	Flow pattern for El=2020 at different conditions. The flow direction is from left to right	59
4.11	Flow pattern for El=3500 at different conditions. The flow direction is from left to right	60
4.12	Flow pattern for El=5000 at different conditions. The flow direction is from left to right	61
4.13	Vortex generation and growing inside a micro-channel	62
5.1	Flow pattern map resulting in different flow regimes	66

List of Tables

3.1	PolyMax™ PC technical information	15
3.2	PC 54 properties	16
3.3	Important dimensions of nozzle geometry	28
3.4	Real dimensions of the microfluidic channels taken in SEM analysis	36
3.5	Width/Depth ratio between each set of micro-channels	43
4.1	Viscosity depending on flow rate and shear rate	46
4.2	Crossing frequency and relaxation time of PC54	47
4.3	Dimensionless numbers for the 3D printing nozzle printing a PC54 polymer	47
4.4	Viscosity, relaxation time and density of PAA samples	50
4.5	Elasticity number for lower concentration PAA samples in different scales channels	50
4.6	Comparison between the PC and 400ppm dimensionless numbers	50
4.7	Relaxation time for 1000,2000 and 10000ppm PAA samples	51
4.8	K coefficients for each microfluidic channel	52
4.9	Density for PAA+water samples at 20°C	52
4.10	Dimensionless numbers for 1000 ppm PAA sample	52
4.11	Dimensionless numbers for 10000 ppm PAA sample	53
4.12	Dimensionless numbers of several printing conditions and of the various testing points	54
4.13	Experimental points and their corresponding dimensionless numbers exhibiting a laminar profile	63
4.14	Different polymer that can create a laminar profile inside a FDM 3D printing nozzle with the current geometrical configuration	64

Symbols and abbreviations

Symbol	Description	Units
a_t	Shift factor	
D_c	Contraction Diameter	m
D_u	Upstream Diameter	m
De	Deborah Number	
$De_{channel_{max}}$	Deborah number in microfluidic channel using a maximum velocity approach	
$De_{channel_{shear}}$	Deborah number in the microfluidic channel using a shear flow approach	
$De_{real_{max}}$	Deborah number in the real prototype using a maximum velocity approach	
$De_{real_{shear}}$	Deborah number in the real prototype using a shear flow approach	
El	Elasticity Number	
G'	Storage Modulus	Pa
G''	Loss Modulus	Pa
G^*	Complex Shear Modulus	Pa
H	Gap in rheometer	m
h	Microfluidic channel depth	m
I	Inertia	Nms^2
k_c	K coefficient for the contraction	
k_u	K coefficient upstream of the contraction	
L	Characteristic length	m
M_0	Torque resolution	Nm
Q	Flow Rate	ml/h
R	Radius	m
Re	Reynolds Number	
$Re_{channel}$	Reynolds number in the microfluidic channel	
Re_{real}	Reynolds number in the real prototype	
T	Temperature	°C
T_m	Melting Temperature	°C
T_g	Glass Transition Temperature	°C
T_0	Reference Temperature	°C
V	Velocity	m/s
V_c	Velocity at the contraction	m/s
V_u	Velocity upstream at the contraction	m/s
w_c	Width of the nozzle contraction	m
w_u	Width upstream of the contraction	m
Wi	Weissenberg Number	

Greek Symbols	Description	Units
δ	Loss factor	
δDe	Uncertainty in Deborah number	
$\delta \eta$	Uncertainty in analogue fluid viscosity	
$\delta \lambda$	Uncertainty in analogue fluid relaxation time	
δRe	Uncertainty in Reynolds number	
δQ	Uncertainty in flow rate	
$\delta \rho$	Uncertainty in density	
δw_c	Uncertainty in the microfluidic channel contraction width	
δw_u	Uncertainty in the microfluidic channel upstream width	
δWi	Uncertainty in Weissenberg number	
$\dot{\epsilon}$	Strain Rate	
η	Viscosity	Pa.s
$\dot{\gamma}$	Shear Rate	1/s
μ	Shear Viscosity	Pa.s
λ	Relaxation time	s
λ_{max}	Maximum relaxation time	s
ω	Frequency	rad/s
ρ	Density	kg/m^3
T	Torque	Nm
τ	Shear Stress	Pa
θ	Angular Displacement	°

Abbreviations	Description
3D	Three-dimensional
ABS	Acrylonitrile butadiene styrene
AM	Additive manufacturing
ASTM	American Society for Testing and Materials
CAD	Computer Aided Design
CEFT	Transport Phenomena Research Center
CTE	Coefficient of thermal expansion
FCUP	Faculdade de Ciências da Universidade do Porto
FDM	Fused Deposition Modelling
FEUP	Faculdade de Engenharia da Universidade do Porto
ISO	International Standardization Organization
MFI	Melt flow Index
MNTEC	Micro and Nanofabrication Unit
PAA	Polyacrylamide
PC	Polycarbonate
PDMS	Polydimethylsiloxane
PLA	Polylactic acid
RPM	Rotation per minute
TMCS	TriMethylChloroSilane

Chapter 1

Introduction

1.1 Motivation

Additive manufacturing (AM) is a cluster for developing technologies that produce layer-by-layer parts, one section at time [1]. There are several AM techniques, and depending of its application and the material used, a specific technique could be more interesting than other. AM's influence can expand to other areas such as medicine, education, architecture and others [2].

One of the most used rapid prototyping or additive manufacturing technologies consists of extrusion deposition processes, such as Fused Deposition Modelling (FDM) [3]. In this process a molten thermoplastic filament is heated in a liquefier and extruded through a nozzle orifice depositing the material into layers, forming a 3D part [4]. The high flexibility of this process and its low investment costs make it a potential technology for future customized products close to its using propose [5]. The most common thermoplastic materials used in this type of process are those who have a low melting temperature and allow a high productive rate, such as ABS and PLA [6]; however its mechanical strength is lower when compared to conventional fabrication techniques and its properties can change depending on loads direction and composite matrices [4, 7, 8].

One of the main problems with FDM is the so called annular backflow, as shown in figure 1.1 where the polymer melt can flow back up the annular region between the filament and the liquefier walls and cool outside of it, which could cause a major blocking problem. Gilmer et.al. [9] developed a mathematical model which predicts a material propensity to backflow, with several properties contributing to this fact namely the filament diameter and the shear-thinning behaviour of the material; however, it was not performed any experimental work to verify this model.

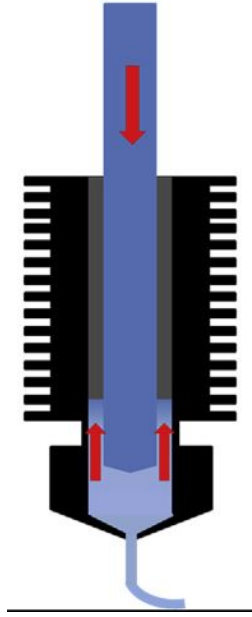


Figure 1.1: Sketch of the annular backflow problem [9]

It is well known in Microfluidics, the field of science studying the flow through channels with at least one characteristic length scale below 1mm, that in the flow of viscoelastic fluids the elastic forces become dominant and the inertial ones become residual, due to its small characteristic length scale [10]. So if we analyse this problem in a perspective of a viscoelastic fluid through a microfluidic contraction-expansion geometry a more interesting result could be achieved as shown in by Evans and Walters [11], where is observed in shear-thinning and high viscosity fluids in planar geometries the emergence of vortices upstream of the nozzle, with the contraction ratio and the elasticity of the fluids contributing for the enhancement of these vortices. This was also verified for Boger fluids (elastic fluids showing no shear thinning behaviour [12]), as shown by M. A. Alves et.al. [13] and by Campo-Deaño et.al. [14] who proved that the vortex generation was produced mainly due to elastic effects independently of inertial effects.

1.2 Objectives and structure

This work is going to analyse the backflow problems in a FDM 3D printing using microfluidic techniques and analogue fluids that at room temperature replicate the flow conditions of the molten polymer inside the 3D printers nozzles. This thesis divided into 3 main parts: Chapter 2 where is done an review about the different Additive Manufacturing techniques and how rheology and microfluidics could have an impact in recreating the printing conditions; Chapter 3 where is reported all the techniques used to perform a rheological characterization of the analogue fluids. Analysis of the real flow and the flow inside the micro channels has been also developed; Chapter 4 where the results of the rheological characterization will be displayed and where all the flow conditions

will be pictured and analysed and finally Chapter 5 where conclusions were drawn based on the different flow path pattern.

Chapter 2

State of the art

2.1 Additive Manufacturing

AM is commonly named 3D printing and represents a form of rapid prototyping [15]. From a 3D CAD file it is possible to create a physical 3D model providing a platform for the development of complex structures with relative ease. The main characteristic of 3D printing is that models are built by adding material layer-by-layer. The thinner the layer, the more accurate the final part will be, but it will take more time to be produced. Based on the ASTM 52900:2015 standard, AM processes can be classified into seven categories [16].

1. Binder Jetting

- Powder particles are joined together by the selectively depositing a liquid bonding agent and a three-dimensional part is created by gluing the particles together

2. Directed Energy Deposition

- Energy is directed into a small region to heat a substrate and melt material that is being deposited. The high power-density laser is focused on a continuous stream of metal powder.

3. Material Extrusion

- Liquefied material is pushed out through a nozzle when constant pressure is applied. The extruded material will deposit at constant speed and fully solidify to the plate.

4. Material Jetting

- Liquid droplets are deposited on the working platform to partially soften the previous layer of material and solidify as one piece.

5. Powder bed fusion

- A thermal source such as laser is used to induce partial or full fusion between powder particles followed by a roller or blade re-coater to smooth another powder layer

6. Sheet lamination

- Material sheets are either cut by using laser or combined by using ultrasound

7. Vat photopolymerization

- Photocurable resins are exposed to laser and undergo chemical reaction to become solid.

In this work we are going to focus our attention on Fused Deposition Modelling (FDM) which is included in the Material Extrusion category.

2.2 Fused Deposition Modelling

FDM is the most recognised and the most widely used process of 3D printing due to its simplicity in constructing objects, being open sourced, and have a outstanding compromise between size, quality of the objects and cost when compared to other technologies [17]. By 2018, FDM printing represented 66% of all 3D printing market [18]. FDM 3D printers have four main elements that are essential to this process: the plastic filament, the material feed mechanism, the print head and the build plate.



Figure 2.1: Key components in FDM 3D printing [19]

- Plastic Filament

The typical materials used are amorphous thermoplastic polymer filaments, being acrylonitrile butadiene styrene (ABS) and polylactic acid (PLA). To proper choose a thermoplastic polymer attention must be paid to some properties like melting temperature (T_m), glass transition temperature (T_g) and coefficient of thermal expansion (CTE). All of these properties will affect layer-by-layer adhesion as well the extrusion process [3, 20, 21].

- Feed Mechanism

In small-scale printers, feedstock is simply a loose coil, while in larger manufacturing systems, the feedstock is coiled inside a cartridge to supply the print head.

- Print head

The print head is integrated with the liquefier and may be fixed or replaceable. The liquefier is generally a metal block with a channel for the polymeric filament to go through. The material inside the chamber should be kept in the molten state but not at very high temperatures compared to its melting temperature since it could lead to a quick degradation of the material properties [3, 15]. The size and geometry of the print nozzle is also of extreme importance because it will limit the resolution achieved in a piece and also affect the flow through it [3]. Typical nozzle openings are between 250 and 800 μm [18].

- Build plate

It is important to ensure good adhesion and the correct gap between the build plate and the nozzle in order to establish a good platform to print the various layers. In many cases printers have a heated build plate, in order to ensure that the first layer do not contract due to cooling [22].

The combination of nozzle configuration and the rheological properties of the polymer melt is extremely important because it impacts how the molten polymer flows through it, and this fact has tremendous consequences in the mechanical properties and global quality of the final pieces. Therefore is important to study the rheology of the materials extruded.

2.3 Rheology

Rheology studies the deformation and flow of matter filling the gap between the classical Fluid Mechanics and Solid Mechanics, by dealing with complex fluids such as polymers. Therefore, the constitutive relationships between stress and deformation for these materials differ from Newtonian law and so they are called non-Newtonian fluids [23].

$$\tau \neq \mu \dot{\gamma} \quad (2.1)$$

where τ is the shear stress, μ is the shear viscosity and $\dot{\gamma}$ is shear rate.

The rheological behaviour serve to sort complex flow fluids into three categories:

1. Time-independent or Generalized Newtonian Fluids (GNF) - show a non-linear relationships between the shear stresses and applied shear rates, where viscosity is typically represented by a function of the shear rate [24].
2. Time-dependent fluids - shows further dependence on the duration of shearing and kinematic history, that is, in these types of fluids apparent viscosity depends on the time of

applied shear along with strain train rate. Such types of liquids are regarded as complex non-Newtonian fluid. It is recognized that there are two main classes of time-dependent fluids: (a) thixotropic and (b) rheopectic [25, 26]

3. Viscoelastic Fluids (VEFs) - exhibit simultaneously properties of elastic solids and viscous liquids, and therefore a characteristic relaxation time (λ) [26]. Viscoelastic fluids typically exhibit a dependency of the viscosity with the applied shear rate

2.3.1 Viscoelastic Fluids

Viscoelastic fluids simultaneously express elastic and viscous properties. These effects are due to a partial memory. Fading memory is exhibited by polymers and it impacts manufacturing processes. When the stress is removed, the stress inside the fluid is still present for some time, which is expressed by a characteristic relaxation time (λ) [23, 27].

The dependency of viscosity with shear rate allows the definition of different rheological behaviours in shear thinning and shear thickening as shown in figure 2.2. Most viscoelastic liquids are polymer melts or solutions and therefore are inherently shear thinning. However, there is a class of viscoelastic fluids, known as Boger fluids, in which the viscosity is nearly independent of the shear rate which is not going to be studied in this project.

Materials for extrusion in AM processes are typically shear thinning and so a more incisive study was carried out in this topic.

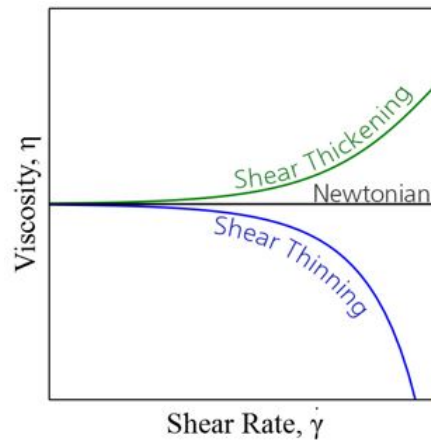


Figure 2.2: Viscosity as function of shear rate [28]

2.3.1.1 Shear Thinning

Shear thinning is characterized by viscosity (η), that gradually decreases with increasing shear rate ($\dot{\gamma}$).

In polymers at rest, long filament molecules contract and become entangled. Under shear, their shape become ellipsoid, aligning with the shear direction. As individual molecules have less flow

resistance than entangled superstructures, the result is a shear-thinning behaviour with viscosity decreasing at higher shear rates [29].

Since viscosity also depends on temperature, it is important to establish a viscosity master curve at an arbitrary reference T_0 . This master curve is built by combining viscosity-shear rate plots for a variety of temperatures T with a shift factor that is given by [30]:

$$a_T = \frac{\eta(T)T_0\rho_0}{\eta(T_0)T\rho} \quad (2.2)$$

where ρ is the density, η is the viscosity at temperature T , ρ_0 and $\eta(T_0)$ at reference temperature T_0 .

The ratio $T_0\rho_0 / T\rho$ is about unity for small temperature differences so it can be neglected. Thus, the shift factor can be rewritten simply as [30]:

$$a_T \approx \frac{\eta(T)}{\eta(T_0)} \quad (2.3)$$

The temperature dependence of a_T can be described by using an Arrhenius dependence of the form:

$$a_T = \exp \left[\frac{\Delta H}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \quad (2.4)$$

where ΔH is the activation energy, which characterizes the energy needed by the molecules to be set in motion against the frictional forces of the neighbouring molecules, and depend on molecular parameters of the polymer [31]; R represent the universal gas constant. Then, the master curve, for shear viscosity can be determined after reducing the viscosity and shear rate.

$$\eta_r = \eta(T_{ref}) = \frac{\eta(T)}{a_T} \quad (2.5)$$

$$\dot{\gamma}_r = \dot{\gamma}(T_{ref}) = a_T \dot{\gamma}(T) \quad (2.6)$$

2.3.1.2 Dimensionless numbers

The relaxation time is the time that a viscoelastic fluid is deformed (flows) after the stress is removed. For example, Newtonian fluids subjected to stress they deform and when the stress is removed the deformation stops [23]. In other words, the relaxation time is related to the amount of elastic energy being stored by the fluid.

This property is responsible for the definition of Deborah and Weissenberg number. The Deborah number gives information how a particular material will behave in a given time period. It is used to estimate the elastic effects during flow. It is generically defined by

$$De = \frac{\text{Relaxation time}}{\text{Characteristic flow time}} = \frac{\lambda}{T} \quad (2.7)$$

where λ is the relaxation time and T is a characteristic flow time. A Deborah number of zero represents a viscous fluid and a Deborah of ∞ an elastic solid.

The Weissenberg number is can be defined as:

$$Wi = \frac{\lambda V}{L} \quad (2.8)$$

where λ is the relaxation time, V is the velocity and L is the characteristic length. It can be described as a the ratio of elastic to viscous forces in a flow [24]. In steady simple shear flow the Weissenberg number can be described as:

$$Wi = \frac{\text{elastic forces}}{\text{viscous forces}} = \frac{\tau_{11} - \tau_{22}}{\tau_{12}} = \frac{\lambda \eta \dot{\gamma}^2}{\eta \dot{\gamma}} = \lambda \dot{\gamma} \quad (2.9)$$

where $\dot{\gamma}$ is the shear rate and λ is the relaxation time. Flows in which the Wi are very small, elastic effects are negligible [24, 32]. Both dimensionless numbers can be described by other formula, depending on the geometry of the flow.

Although in many flows the Weissenberg and Deborah number, have the same formulation but they have a clearly different meaning [14]. The Weissenberg number is only used in flows where the strain rates are uniform. That is encountered in viscometric flows and theoretical analysis, but rarely observed in any practical application. The Deborah number is used in a non uniform strain rates, which is the case in any practical experiment [25, 32].

To fully define the flow conditions is also necessary to establish the Reynolds number which represents the ratio of inertia to viscous forces, and is generally defined as :

$$Re = \frac{\text{Inertial forces}}{\text{Viscous forces}} = \frac{\rho V L}{\eta} \quad (2.10)$$

which ρ is the density of fluid; V is the velocity L is the characteristic length of the channel and η the viscosity. It is also helpful to define an elasticity number, El , typically defined by:

$$El = \frac{Wi}{Re} = \frac{\lambda \eta}{\rho L^2} \quad (2.11)$$

This number represents a ratio of elastic to inertial effects, and is independent of fluid kinematics [33]

2.4 Contraction Flows

The extrusion of molten polymers in industrial processing operation dates back to 1840 [34]. However, the fundamental research related to this subject is considerably more recent. Many of the early works were related to rubber compounds and in later 1940s [35] were refocused for thermoplastic polymer melts. Nowadays, extrusion of thermoplastic polymers represents one of the most rapidly growing processes in the past decades. However in this technology there are many types of unique flow instabilities, including upstream vortices. These instabilities come from the viscoelastic nature of the polymer melts. The extrusion flow can be seen as a very simple axisymmetric or planar geometry in which a fluid flows through a narrow capillary. Nevertheless, there are some crucial features directly linked with the viscoelastic behaviour of the polymer melts that

consequently leads to flow instabilities. First, high shear stress at the contraction of the extruder. Second, strong transient uniaxial extensional flow caused by intensive acceleration due to an increased flow rate through the contraction and of course geometrical singularities namely a sharp change of direction and sharp salient edges. As a result of these particularities a funnel shaped flow emerges with recirculating material in the corners. The recirculation flow is superimposed on the major primary flow and it is commonly termed as vortices or recirculation zone [36] as shown in figure 2.3:

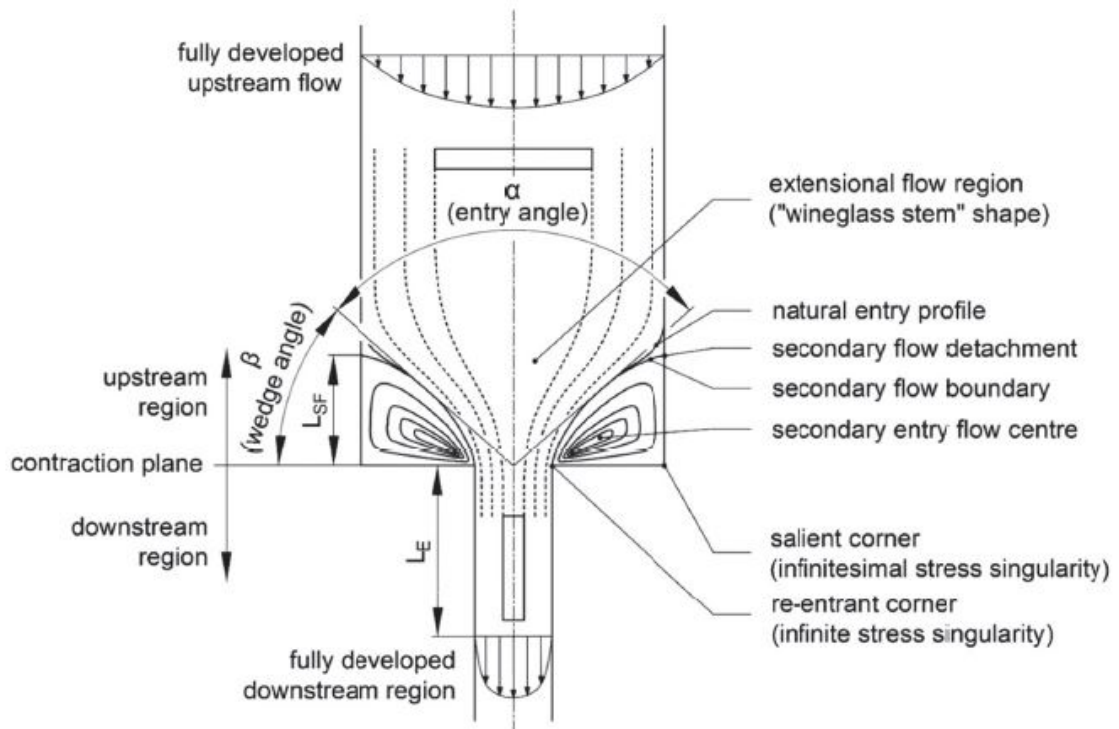


Figure 2.3: Schematic streamwise view of an abrupt contraction flow [36]

Several studies have been conducted through the years, but the first major research was conducted by James L. White et. al. [37], who investigated a wide range of polymer melts including low and high densities of polyethylene, polystyrene, nylon 66, etc. Upstream vortices were photographed in many of these polymers as shown in figure 2.4.

The following research studies tried to find an answer for the formation and development of these upstream vortices. The research conducted by Baird et.al. [38] and Munstedt et.al. [39] revealed that not only that the vortices growth could not be attributed only to shear and normal stress alone but also to the presence of large extensional stresses at the entry region. Finally Hertel and Munstedt [40] concluded that the vortex formation was related to the occurrence of strain hardening, in other words, fluids with a shear thinning while extensional thickening behaviour potentiate an unbalanced flow in terms of the momentum equation, leading to a reorientation of the fluid ultimately leading to the vortices formation.

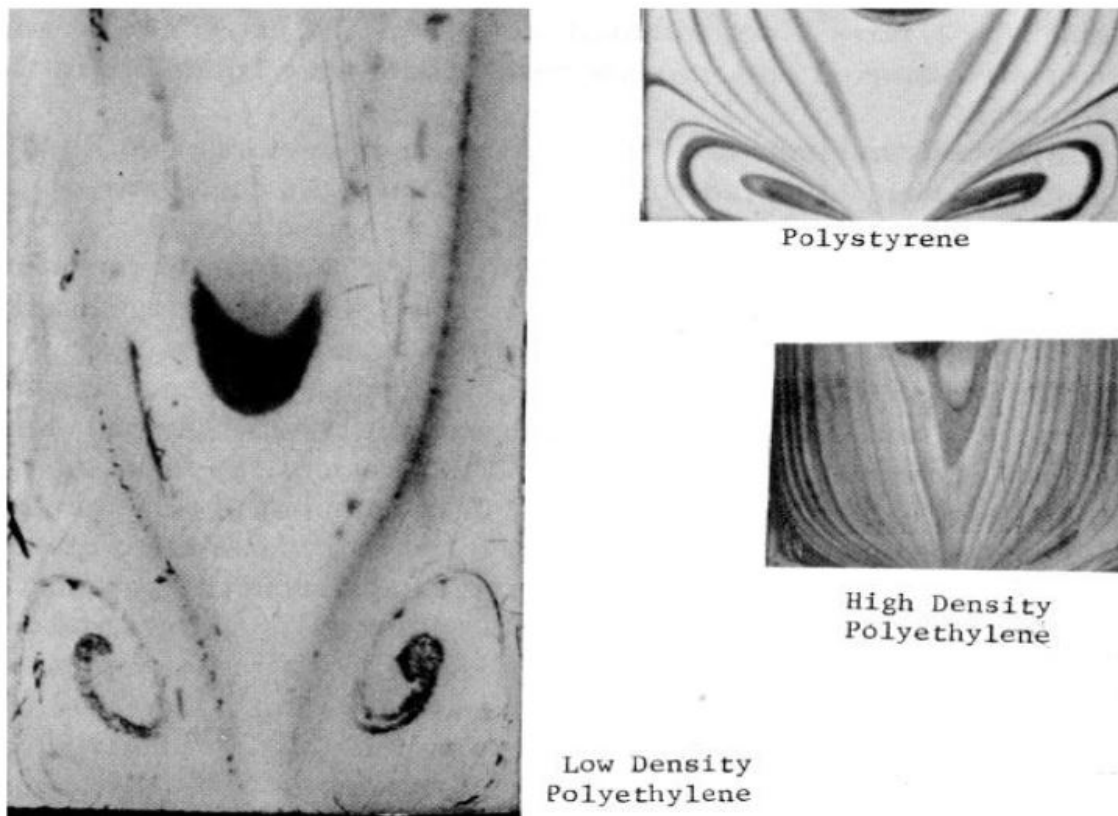


Figure 2.4: Entrance flow pattern in three different melts [37]

If we analyse the FDM 3D printing process, it is very similar to a classical extruding process, that is, a polymer melt flows through a nozzle, generally with an abrupt change in the geometrical configuration. However very few studies have been conducted in this area regarding the visualizations of the flow profile. So this work is going to analyse the flow behaviour inside a 3D printing nozzle by using a microfluidic approach since it can replicate the upstream vortices as shown in previous works not only in Boger fluids [14] but also in viscoelastic fluid exhibiting shear thinning behaviour [41].

2.5 Microfluidics

Since FDM 3D printing nozzles can vary from $250\mu\text{m}$ up to $800\mu\text{m}$, microfluidics can contribute for a better understanding of flow through the nozzle and therefore a better printing quality [18]. Microfluidics is the science and technology which deals with geometries in the scale of microns. Flows within geometries with characteristic length scale of less than 1mm can be considered in this group [14]. This technology has been developed over the past few decades and nowadays is being implemented in a wide range of industries from biology and pharmaceuticals up to manufacturing with a particular importance in 3D printing [42].

Joining the effects of microfluidics with rheology and some particularities arise mostly with the dimensionless numbers. Small scale lengths results in very small Reynolds numbers ($Re \ll 1$), in these cases it is possible to neglect inertia effects since viscous effects dominate the flow [43]. This particularity enables the study of fluid elasticity without the inertia effects giving an platform for performing rheological characterization beyond the actual macro-scale rheometers. Microfluidic devices can produce high shear rates, high Wi or De numbers at low Re numbers. This is very important in the case of low viscosity elastic fluids whose elastic character only displays at these condition [44, 45].

Non-Newtonian fluids-flows at microscale are difficult to describe mathematically due to their viscosity which is dependent of the shear rate and their elastic behaviour. The nature of the flow changes from a simple shear flow near the walls to a complex extensional flow near the centreline in geometries presenting contractions and expansions. Since non-Newtonian fluids can have elastic behaviour and at the same time exhibit non-linear viscous effects like shear-thinning behaviour, it is particularly difficult to study these flows in isolation from other effects [14].

2.5.1 Micro-device Fabrication

There are different types of micro-fabrication techniques, each with their limitations which will determine the shape and material of the micro-channels. The most common materials used are the ones that provides a good platform to develop cheap and complex micro-fluidic devices such as [24]:

- Silicon-based materials

These devices are based in Micro-Electro-Mechanical Systems (MEMS) methods. MEMS devices typically have 1-10 μm minimum features but this process is quite complex and the fabrication time is substantial.

- Paper materials

It is an attractive solution mainly because is a cheap, light-weight and disposable material which represents an advantage when compared with others, but small imprecise volumes limit the precision of these devices. Moreover their design is suited for individual testing.

- Polymer materials

These materials reduces the fabrication time while providing a simple and cost effective method. They exhibit flexibility, chemical inertness and low toxicity, being commonly used for fabricating the micro-fluidic devices.

Within the polymer materials group it is possible define two sub-groups: Thermoplastics and Elastomers.

Thermoplastic materials are particularly interesting for large-scale industrial productions and have important properties for a microfluidic study like its low chemical absorption, biocompatibility and high transition temperature [46]. For a rapid prototyping this material become expensive and so for a small number of uses a Elastomer is generally used. These materials are inexpensive, enables a simpler method to fabricate devices although requires a significant amount of time to produce it. One of the mostly used elastomer is Polydimethylsiloxane (PDMS) because it has favourable mechanical properties and simple manufacturing through casting and curing onto a microscale mold and sealing to a wide range of materials [24, 47].

There are several techniques to produce elastomeric devices such as Replica Micromolding, Microcontact Printing (μ CP), Microtransfer Molding (μ TM) and Microcapillary Molding (MIMIC), but the one that we are gonna focus our attention is Soft Lithography, which is based on replica micromolding and is the one available in the laboratory therefore, it will be used in this work.

2.5.1.1 Soft Lithography

Soft lithography can be viewed as a prolongation of photolithography. After the definition of a mask in a CAD program, the mask leads to a production of a master mold to be used for the creation of the microfluidic device. Generally this master is made of a SU-8 photoresist, a photocurable epoxy, on a silicon wafer. Once a master is fabricated it is possible to form PDMS channels by replica molding. The PDMS and a curing agent are mixed in a 10:1 ratio in weight. The mixture is then poured onto the mold. After cooling the PDMS can be peeled off. Finally the PDMS can be sealed onto glass to create the fluidic device, as shown in figure 2.5 [48]. A more detailed explanation of all the stages of fabrication will be conducted in Chapter 3.

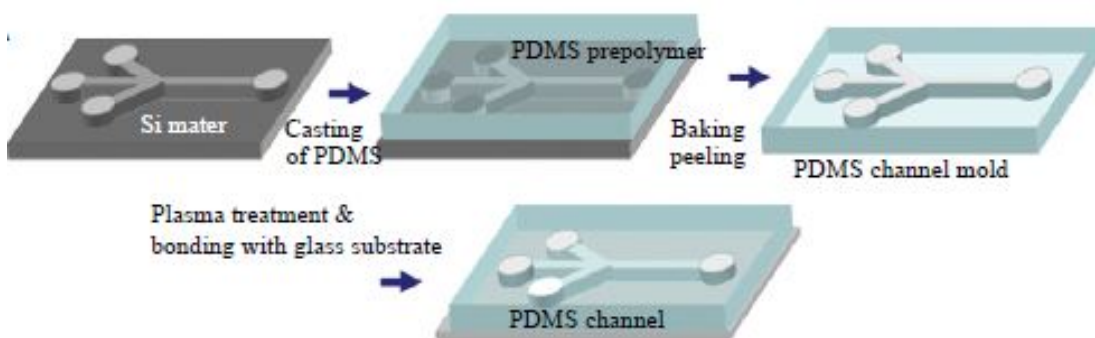


Figure 2.5: Process for creating PDMS microfluidic channels [47]

Chapter 3

Materials and Methods

3.1 Rheological characterization of the polymeric material for 3D printing

The material used in the 3D printing process and the central focus of our study is a Polycarbonate. Polycarbonate is a polyester containing repeating carbonate groups. A number of polycarbonate have been produced from phenols but the most used is the phenol-A revealing the best overall physical properties. They are distinguished by their unique combination of properties, especially high heat resistance, dimensional stability and good mechanical properties [49]. The polycarbonate used in the 3D printing is the PolyMax™ PC from Polymaker that have the printing and mechanical characteristics presented in table 3.1:

Due to technical limitations, (the rotational rheometer at CEFT is not equipped with an oven to work with molten polymer) it was not possible to perform a proper rheological characterization of this material. To overcome this problem, a similar polycarbonate was selected from the book "Handbook of Polycarbonate Science and Technology" [51]. The criterion for selecting a similar polycarbonate to the real one (PolyMax™ PC) was based on the similarity of Melt Flow Index (MFI) values. MFI is defined as the weight of polymer extruded in ten minutes through a capillary of a specific diameter when applied a specific pressure and temperature. This parameter can have a direct correlation to the viscosity of the melt [52].

Table 3.1: PolyMax™ PC technical information [50]

Density	1.18 – 1.20 (g/cm^3 at 21.5 °C)
Glass Transition Temperature	113 (°C)
Melt Index	6-8 (g/10min) @260°C
Nozzle temperature (printing)	250-270 (°C)
Printing Speed	30 - 50 (mm/s)
Young Modulus	2048 ± 66 (MPa)
Tensile strength	59.7 ± 1.8 (MPa)
Elongation at break	12.2 ± 1.4 (%)

Although MFI experiments were conducted at 300°C. At the typical printing temperature the MFI value will still be inside the range of the PolyMax™ PC MFI values. Table 3.2 gives some information about the chosen melt here described as PC54.

Table 3.2: PC 54 properties [51]

PC 54	
Inherent Viscosity (dl/g)	0.54
MFI (g/10min)	7.4
Mw (g/mol)	60600
Mn (g/mol)	24400
Mw/Mn	2.5

3.2 Analogue fluid

3.2.1 Samples preparation

For the analogue fluids, three types of solutions were prepared. The type A, resulted from mixing Polyacrylamide (PAA) with a molecular weight $M_w = 18 \times 10^6 \text{ g mol}^{-1}$ at different weight concentrations (50, 100, 200, 300, 400, 1000, 2000 and 10000 ppm) into de-ionized water, acting as a solvent, using magnetic stirrers at low speeds in order to prevent any mechanical degradation of the polymer molecules.

The type B was prepared by mixing 50 and 100ppm of PAA samples into glycerol in 90/10 w/w ratio. Type C was prepared using the same polymer concentration in glycerol but with different ratio, 70/30 w/w. Equations 3.1 and 3.2 gives the formulas used to calculate the different weight concentrations values:

$$m_{PAA} = \frac{m_{PAA}}{m_{PAA} + m_{H_2O}} \quad (3.1)$$

$$m_{glycerol} = \frac{m_{glycerol}}{m_{glycerol} + m_{PAAsample}} \quad (3.2)$$

The samples were sealed with a parafilm tape to prevent partial evaporation of the solvent during the mixing process as shown in figure 3.1. The mixing process was carried out for at least two days, with the water/glycerol taking a couple more days to ensure a homogeneous solution.

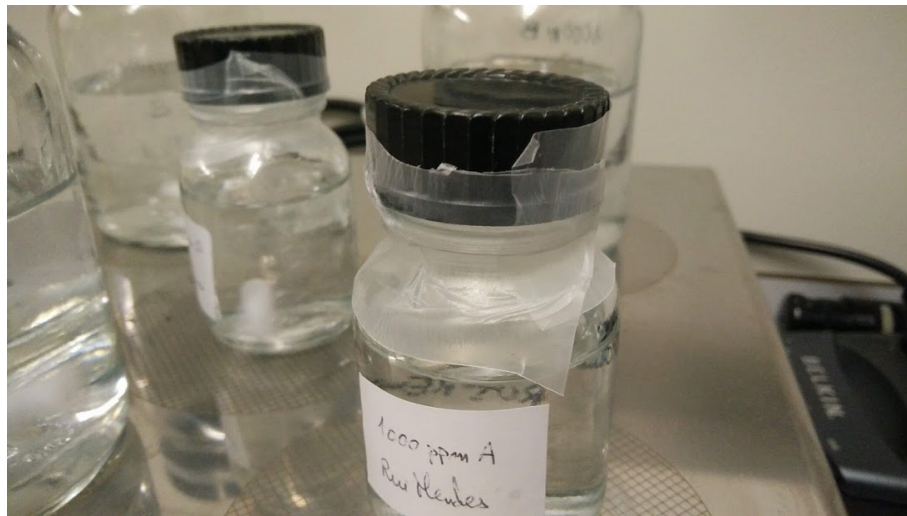


Figure 3.1: Mixing process of the analogue fluid samples

3.3 Rheometry Experiments

Some properties of the analogue fluid can be measured in shear flow. For the shear measurements, experiments were performed on a stress-controlled shear rheometer: Anton Paar, model Physica MCR301 as shown in figure 3.2.



Figure 3.2: Anton Paar, model Physica MCR301 rheometer

For each experiment a plate/plate (PP) configuration, with a diameter of 50 mm, was used simply because by imposing a small gap value (0.1mm) it was possible to collect reliable results at higher shear rates, plus it requires a relative small amount of sample and the cleaning is easy and quick. This geometry is defined by specific standards for measuring systems such as ISO 3219-2 and DIN 53019 [29]

To measure the unknown fluid properties in this geometry configuration we will make some assumptions about the velocity profile. When the upper disk is rotated at a constant angular velocity ω , the velocity profile is:

$$\underline{v} = \begin{bmatrix} 0 \\ v_\theta \\ 0 \end{bmatrix}_{r\theta z} \quad (3.3)$$

Assuming incompressible flow the continuity equation is:

$$v_\theta = A(r)z + B(r) \quad (3.4)$$

where A(r) and B(r) are unknown functions of r. For cylindrical coordinates the boundary conditions are:

$$v_\theta = 0 \quad \text{at} \quad z = 0 \quad (3.5)$$

$$v_\theta = r\omega \quad \text{at} \quad z = H \quad (3.6)$$

Applying these boundary conditions to the equation for the velocity yields

$$v_\theta = \frac{r\omega z}{H} \quad (3.7)$$

The rate-of-deformation tensor is then

$$\underline{\dot{\gamma}} = \nabla \underline{v} + (\nabla \underline{v})^T \quad (3.8)$$

$$\underline{\dot{\gamma}} = \begin{bmatrix} 0 & \frac{\partial v_\theta}{\partial r} - \frac{v_\theta}{r} & 0 \\ \frac{\partial v_\theta}{\partial r} - \frac{v_\theta}{r} & 0 & \frac{\partial v_\theta}{\partial z} \\ 0 & \frac{\partial v_\theta}{\partial z} & 0 \end{bmatrix}_{r\theta z} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & \frac{r\omega}{H} \\ 0 & \frac{r\omega}{H} & 0 \end{bmatrix}_{r\theta z} \quad (3.9)$$

$$\dot{\gamma} = |\underline{\dot{\gamma}}| = \frac{r\omega}{H} \quad (3.10)$$

where H is the gap between disks, r the radius of the plate and ω the angular velocity. The assumption of nearly unidirectional flow is best at the rim, $r=R$, and therefore viscosity can be

calculated from

$$\eta = \frac{-\tau_{21}}{\dot{\gamma}_0} = \frac{-\tau_{z\theta}|_{r=R}}{\dot{\gamma}_R} \quad (3.11)$$

Now is important to define τ in order to establish an expression for the viscosity. Although is possible to measure τ is simpler to measure the total torque required to turn the upper disk. The torque is given by:

$$\mathbf{T} = \int_A (\text{stress})(\text{lever arm}) dA \quad (3.12)$$

$$\mathbf{T} = \int_0^R (-\tau_{z\theta}|_{r=R})(r)(2\pi r dr) \quad (3.13)$$

Since τ can be written as a function of viscosity as shown in equation 3.9, thus

$$\mathbf{T} = 2\pi \int_0^R \eta \dot{\gamma} r^2 dr \quad (3.14)$$

Taking the derivative and replace r in the integral with $\dot{\gamma}$, using $\dot{\gamma} = \dot{\gamma} r / R$, it takes

$$\left(\frac{\mathbf{T}}{2\pi R^3} \right) \dot{\gamma}_R^3 = \int_0^{\dot{\gamma}_R} \eta \dot{\gamma}^3 d\dot{\gamma} \quad (3.15)$$

$$\frac{d}{d\dot{\gamma}_R} \left[\left(\frac{\mathbf{T}}{2\pi R^3} \right) \dot{\gamma}_R^3 \right] = \int_0^{\dot{\gamma}_R} \frac{\partial}{\partial \dot{\gamma}_R} (\eta \dot{\gamma}^3) d\dot{\gamma} + \eta(\dot{\gamma}_R) \dot{\gamma}_R^3 \quad (3.16)$$

The first term on the right side is zero, and after rearrangement the viscosity measured is:

$$\eta(\dot{\gamma}_R) = \frac{\mathbf{T}/2\pi R^3}{\dot{\gamma}_R} \left[3 + \frac{d \ln(\mathbf{T}/2\pi R^3)}{d \ln(\dot{\gamma}_R)} \right] \quad (3.17)$$

The storage and loss modulus can also be measured with this geometry in Small Amplitude Oscillatory Shear (SAOS) due to the following equations:

$$G' = \eta'' \omega \quad (3.18)$$

$$G'' = \eta' \omega \quad (3.19)$$

The SAOS material functions $\eta'(\omega)$ and $\eta''(\omega)$ can be related to the torque amplitude and the phase lag δ . The expression that describe this relation are in Bird et al. [30] and can be written as:

$$\eta' = \frac{2H\mathbf{T}_0 \sin \delta}{\pi R^4 \omega \theta_0} \quad (3.20)$$

$$\eta'' = \frac{2H\mathbf{T}_0 \cos \delta}{\pi R^4 \omega \theta_0} \quad (3.21)$$

with T_0 as the torque amplitude, R as the plate radius, θ_0 as the angular displacement of the plate and δ as the phase lag.

3.3.1 Start-up and Viscosity curves

The first test which could give some information about some characteristics of the fluids prepared was the Viscosity Curve. This experiment should exhibit in a viscosity-shear rate plot the desired shear-thinning behaviour of the samples. In order to obtain a viscosity curve through a steady-state condition is very important to guarantee that this condition is verified. To do so, the transient response of every sample was measured to determine the minimum time required to reach the steady state. The evolution of the transient stress with time features two regions as shown in figure 3.3: the first one between the onset of the transient test and the maximum shear stress, and the second one ranging between this maximum and the steady state shear stress. The first region, where is reached the maximum value of stress, also called stress overshoot τ_{max} is a consequence of viscoelastic response of the polymer. The stress overshoot is related to the energy necessary to produce significant structural breakdown when the shear flow begins [53].

The steady-state viscosity curves were performed for a shear rate sweep from 0.1 up to 100000 1/s, with a duration in accordance with the step curves previously done.

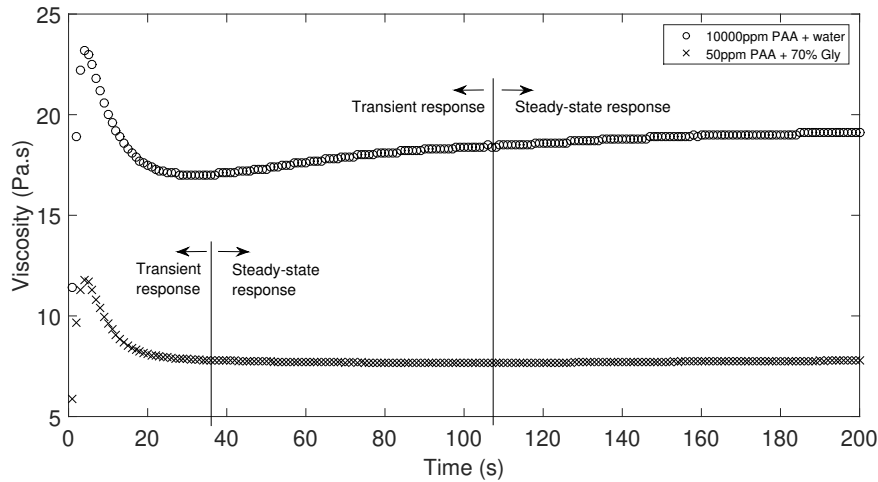


Figure 3.3: Star-up Curve for 10000ppm PAA+water and 50ppm PAA+water with 70% Glycerol

3.3.2 Small Amplitude Oscillatory Shear (SAOS) tests

Another form to characterize viscoelastic fluids is by oscillatory shearing motion. By utilizing the viscoelasticity principles it is possible to correlate mechanical behaviour with molecular structure. The quantity of interest is the complex shear modulus G^* given as [54]:

$$G^* = G' + G'' \quad (3.22)$$

where G' is the storage modulus, which represents the elastic portion of the viscoelastic behaviour and G'' the loss modulus which represents viscous portion of the viscoelastic behaviour. The elastic component is the portion of energy that is stored in the material that is being deformed. When the fluid is not at stress any more, the storage energy acts as a driving force to curl up the molecules into their original shape. The viscous part is characterized as the dissipated heat energy which is result of internal friction between molecules and particles in a flowing fluid [29].

The ratio of viscous and elastic portion of the viscoelastic deformation behaviour is defined by a loss factor that is given by:

$$\tan \delta = \frac{G''}{G'} \quad (3.23)$$

For ideally elastic behaviour $\delta=0$, for ideally viscous behaviour $\delta=1$

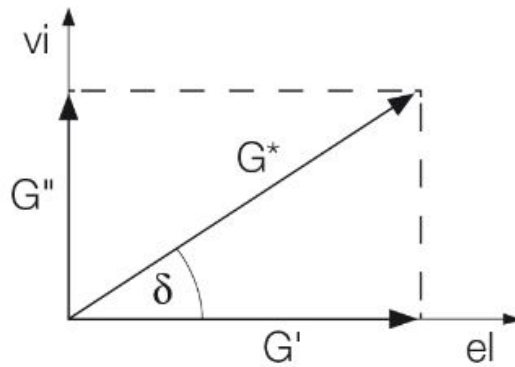


Figure 3.4: Relation between storage, loss modules and complex shear modulus [29]

These tests were performed by subjecting a sample to a deformation with a sinusoidal shape. Typically a sample is placed between two plates equipped with sensors. The first is located in the top plate and detects the strain applied to the fluid as:

$$\gamma = \gamma_0 \sin \omega t \quad (3.24)$$

While the second located in the stationary plate detects shear stress.

$$\tau = \tau_0 \sin(\omega t + \delta) \quad (3.25)$$

The two sines curves, the preset and the response one, oscillate at the same frequency but in viscoelastic behaviour the result show a time lag for the response signal. This lag is the phase shift δ [29].

Oscillatory tests can be divided into two groups. The first one reproduces a linear viscoelastic response, which indicates the test can be carried out without destroying the structure of the sample, typically called Small Amplitude Oscillatory Shear, SAOS. The other one is called Large

Amplitude Oscillatory Shear, LAOS and is defined by a measurable non-linear material functions as shown in figure 3.5.

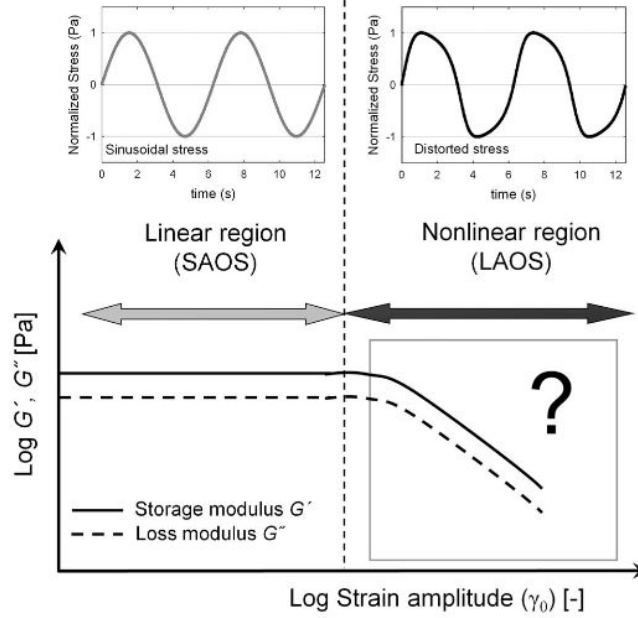


Figure 3.5: Amplitude sweep at a fixed frequency used to determine the linear viscoelastic region [55]

In this work we used the SAOS because the objective was not to break irreversibly the structure of samples but do a rheological characterization of complex fluids allowing a rigorous theoretical foundation of this type of test and so discovering the material functions G' and G'' [55]. To determine the shear stress that divides the linear from the non-linear regimes a amplitude sweep for a wide range of frequencies.

After this procedure, it is possible to perform a frequency sweeps that generally describes the time-dependent behaviour of a sample in the linear range. In this test the amplitude is maintained constant while the oscillation frequency is increased. Short-term behaviour is simulated at high frequencies and long-term behaviour is evaluated at low frequencies. The only condition to perform this test is that the test is carried in the LVE region as discussed previously.

Polymer solutions have a spectrum of relaxation time, related to a intermolecular interactions in the polymeric chain. It can be obtained in frequency sweep tests from the crossover of G' with G'' curves as shown in figure 3.6 where [25]:

$$\lambda = \frac{1}{\omega} \quad (3.26)$$

where λ is the relaxation time and ω is the frequency

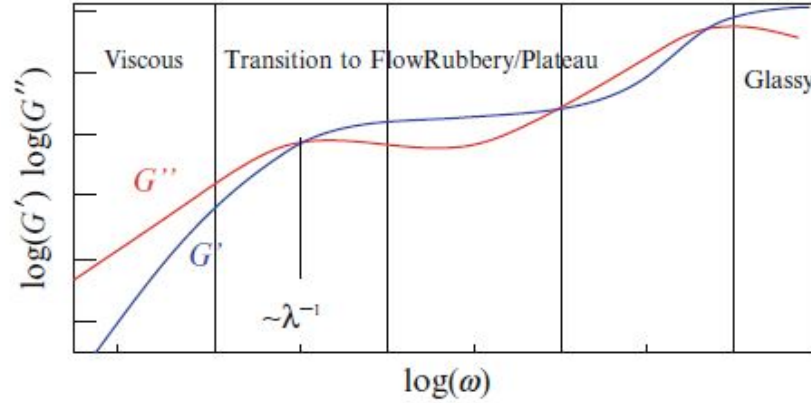


Figure 3.6: Storage and loss modules in a frequency sweep test [25]

However, the determination of the relaxation time (λ) for dilute polymeric solution is very difficult to do, especially due to the solvent low viscosity, which interferes in traditional shear rheological experiments mainly caused by inertial effects [56], which ultimately could lead to non-crossing G' and G'' curves.

The overall response is given as a combination of several modes. Each mode is described in terms of a Maxwell mode which corresponds to a different relaxation time. The relaxation modulus for a Maxwell model is given by:

$$G(t) = G \exp\left(-\frac{t}{\lambda}\right) \quad (3.27)$$

So several modulus can be described as:

$$G(t) = G_e + \sum_i G_i \exp\left(-\frac{t}{\lambda_i}\right) \quad (3.28)$$

Based on the previous equation the relaxation time spectrum $H(\lambda)$, can be defined as

$$H(\lambda) = \sum_i G_i \delta(\lambda - \lambda_i) \quad (3.29)$$

Re-writing equation 3.28 we have:

$$G(t) = G_e + \int_0^{\lambda_{max}} H(\lambda) \exp\left(-\frac{t}{\lambda}\right) \frac{d\lambda}{\lambda} \quad (3.30)$$

where G_e corresponds to the equilibrium modulus, which takes the value of 0 for liquids; and λ as the relaxation time [25]. The $H(\lambda)$ is a non-negative function that is finite in the range between 0 and λ_{max} . The latter corresponds to the longest relaxation time, which is the upper limit in which $H(\lambda)=0$ [57].

3.3.3 Extensional Rheometry

In extensional rheometry, the extensional relaxation time, λ_E is typically the largest in magnitude when compared with the value of any relaxation time measured with other technique [45], so it is fairly to assume that $\lambda_E \approx \lambda_{max}$. A Capillary Breakup Extensional Rheometer (Haake CaBER 1, Thermo Scientific) was used to measure this relaxation time as shown in figure 3.7. In this configuration, the bottom plate is stationary and the other imposes a step strain deformation. In the initial state the plates are separated by a gap h_0 and a sample of fluid is placed between them. To perform the experiment the top plate moves upwards leading to a thinning fluid filament towards a non-equilibrium situation resulting in a thinning process in the central region between the plates. The filament thinning process was recorded using a high speed video camera (Photron FASTCAM Mini UX100), at 1000 fps giving a result as shown in figure 3.8.

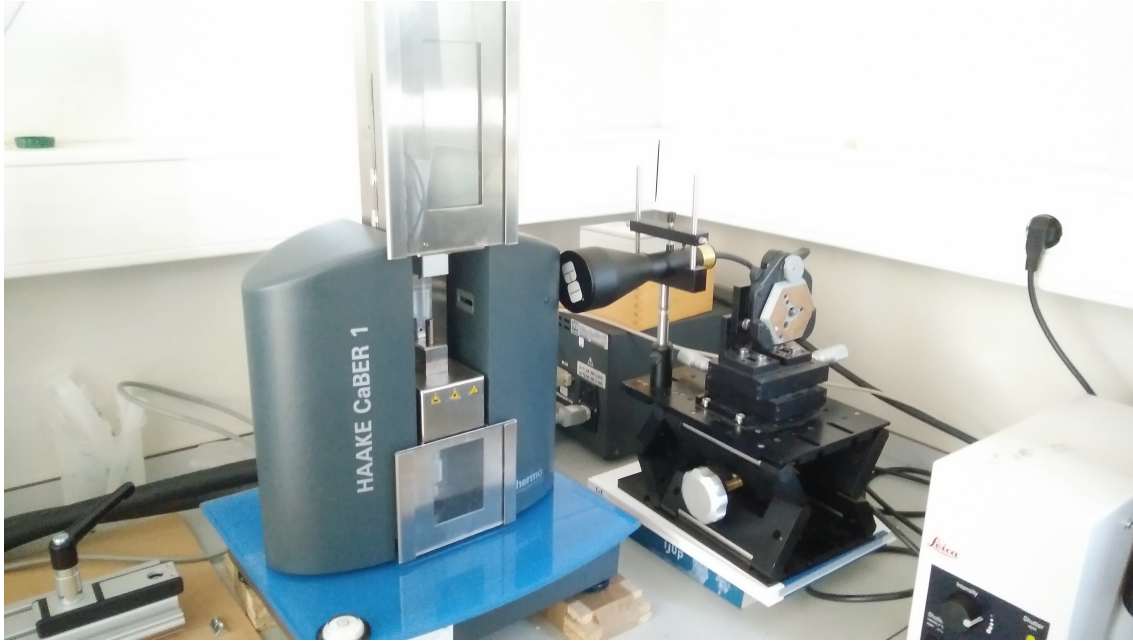


Figure 3.7: Haake CaBER 1, Thermo Scientific

Each set of images has been analysed by means of the Matlab Image Processing Toolbox, which allowed to determine the time evolution of the minimum diameter in the filament thinning process $D_{mid}(t)$. The characteristic shapes of the evolution of $D_{mid}(t)$ for each fluid represent different material properties and the relaxation time of the liquids determined from the exponential decay of the filament diameter [14]. The evolution in the midpoint profile is governed by a force balance which can be described by:

$$D_{mid}(t) = D_0 \left(\frac{GD_0}{4\sigma} \right)^{1/3} \exp\left(-\frac{t}{3\lambda}\right) \quad (3.31)$$

where λ is the characteristic relaxation time of the polymeric liquid. The diameter of the thinning

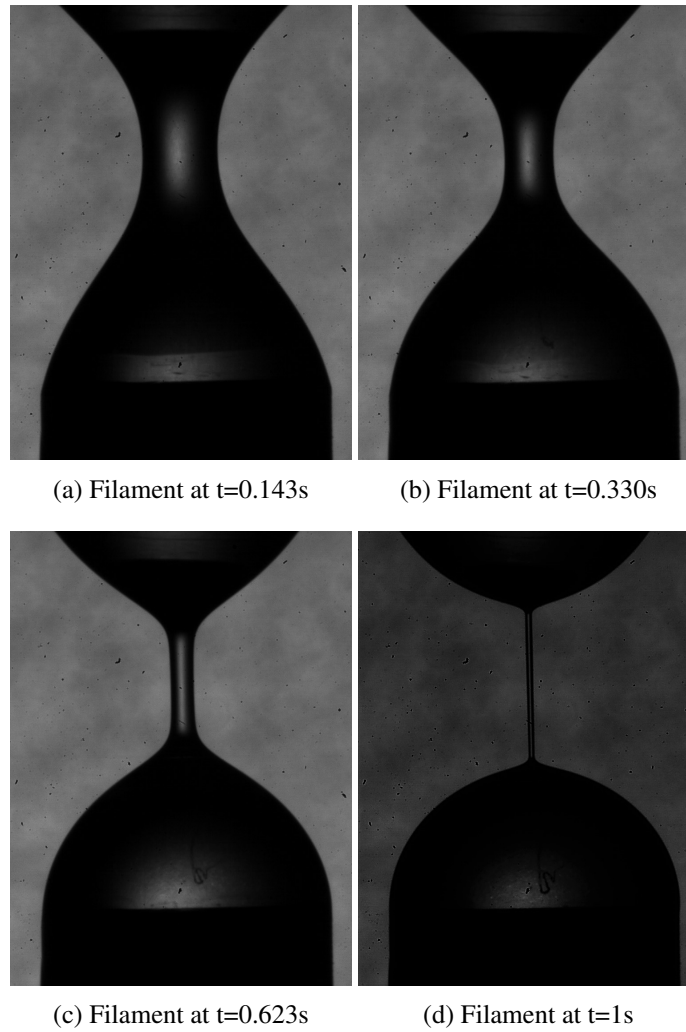


Figure 3.8: Filament thinning process recorded with a high speed camera at 1000 fps

filament decays in time prior to breakup. Moreover, since the necking is only balanced by the viscous resistance, it means that the higher the shear viscosity of the sample, the larger the break-up time is in the CaBER tests [58]. The decay is then computed into the equation 3.31 to determine the fluid maximum relaxation time.

3.3.4 Errors and limits of reliability on shear rheometry

In order to avoid a miss interpretation of the data collected in the rheometer some procedures should be taken in account. The first one is the sample manipulation and the amount inserted for testing. It is recommended to slightly overfill the geometry forming a small bulge at the edge in order to avoid air trapped inside which would affect the measurements. The correct amount according to the norm DIN 51810-1 is presented in the figure 3.9.

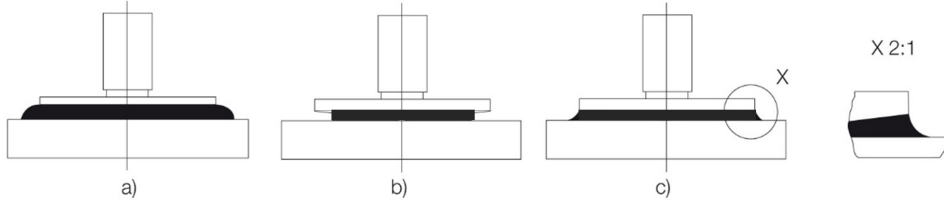


Figure 3.9: Filling of a plate-plate geometry where: a) overfilled, b) underfilled and c) is the correct amount [29]

If the sample is under-filled, it leads to a non-constant contact zone which will affect the measurements. Evaporation and migration of the sample could also lead to a measurement error. Also, the presence of bubbles inside the geometry could lead to an increase of G' at lower angular velocity (ω) which could be comparable to an additional relaxation in the polymer molecules.

It was also important to define a window of data that would guaranty the reliability of measurements. To do so it was established two limits for the viscosity curves. The first one is a minimum value of viscosity from which the results are not affected by the resolution of the rheometer. The equation 3.20 establishes this limit and is defined by [59, 60]:

$$\eta_{min} = \frac{2M_0}{\pi R^3 \dot{\gamma}} \quad (3.32)$$

where M_0 is the torque resolution of the rheometer (1×10^{-7} Nm), R the geometry radius and $\dot{\gamma}$ the shear rate. This limitation especially applies to strain controlled rheometers measuring in the terminal regime while staying in the linear viscoelastic range [60]. A similar low torque slope can be plotted for the storage and loss modulus when performing an amplitude sweep which takes [61]

$$G_{min} = \frac{2M_0}{\pi R^3 \gamma_0} \quad (3.33)$$

where γ_0 is the strain amplitude and G_{min} represents either G' and G'' .

For frequency sweeps the "material torque" should be bigger than "the instrument inertia torque", in other words, the torque created in the material should be bigger than the inertia torque required to impose the deformation. This rule can be written in form of an equation as:

$$\mathbf{T}_{material} > \mathbf{T}_{inertia} \quad (3.34)$$

$$\frac{G\gamma_0}{F_\tau} > I\theta_0\omega^2 \quad (3.35)$$

$$G > I \frac{F_\tau}{F_\gamma} \omega^2 \quad (3.36)$$

given that $F_\tau = \frac{2}{\pi R^3}$ and $F_\tau = \frac{R}{H}$ thus

$$G > I \frac{2H}{\pi R^4} \omega^2 \quad (3.37)$$

where $I=0,0117174 \text{ mNms}^2$ and represents the value of the inertia measurement system that is given by the rheometer software; R is the plate radius, and G represents either G' or G'' .

At high velocities, secondary flows can appear. Even without a turbulent flow, the primary shear flow is overlaid by a secondary flow that is enhanced by the centrifugal force that throws the sample to the borders creating a sort of a vortex. This additional flow creates an dissipation which leads to an increase in torque. This can cause to incorrectly catalogue a fluid as shear-thickening [61]. Experimental limits can be set in order to define a limit for valid data to be assumed as shown in equation 3.38.

$$\eta_{sec} = \frac{H^3 \rho \dot{\gamma}}{12 \tilde{R} R} \quad (3.38)$$

where H is the gap, ρ is the density and $\tilde{R}$ is a parameter ($\tilde{R}$ for onset of secondary flow) [59].

This secondary flow can also be caused by purely inertial effects due to Taylor instabilities. It is also possible to experiment purely elastic instabilities at high Wi/De numbers for elastic liquids in rotational geometries. This effect can be explained by the Weissenberg Rod-Climbing Effect, where a non-Newtonian fluid climbs a rod that is rotating. Rod climbing is due to the non-zero normal stress differences, which forces the fluid up the rod [62]. This effect can also be felt in rheometry, mainly at high shear rates, causing an additional force in the geometry of the rheometer which leads to an increase in the viscosity but like previously pointed this should not suggest an shear thickening behaviour. The data that exhibit this characteristic should not be considered for characterizing a sample.

3.4 Microfluidics

In order to reproduce the geometrical conditions of the 3D printing nozzle it was necessary to replicate the shape of it in a microfluidic device to ensure the maximum reproducibility of the real conditions. To do so it was necessary to perform a multi-step process:

3.4.1 Micro-channel design

Each micro-channel possesses its own inlet and outlet ports. In between them there is a contraction that replicates the cross section of the 3D printing nozzle and a sudden expansion to simulate the expansion of the polymeric material when leaves the nozzle and interacts with the atmosphere, as shown in figures 3.10 to 3.12. To ensure a fully developed condition upstream of the contraction it was necessary to fulfil the condition for laminar flow that is [63]:

$$\frac{L}{D_h} \approx 0.05 Re_D \quad (3.39)$$

where D is the diameter of the channel downstream of the inlet and L the entry length.

Since the device was to be used in a wide range of Reynolds numbers and to guaranty a safety margin, it was considered the fully developed condition for turbulent flow that is:

$$\frac{L}{D_h} > 10 \quad (3.40)$$

Four channels with four different scales (1:1 1:2, 1:4 and 1:8) were produced, as shown in figures 3.11, not only to exactly replicate the geometry but also to scale down the problem in order to mimic the flow conditions of the real printing in terms of Re and De numbers. All micro-channels were designed in a CAD program (Autodesk AutoCAD) under the guidelines and layout constrains imposed by Micro and Nanofabrication Unit (MNTEC), where later they would be materialised.

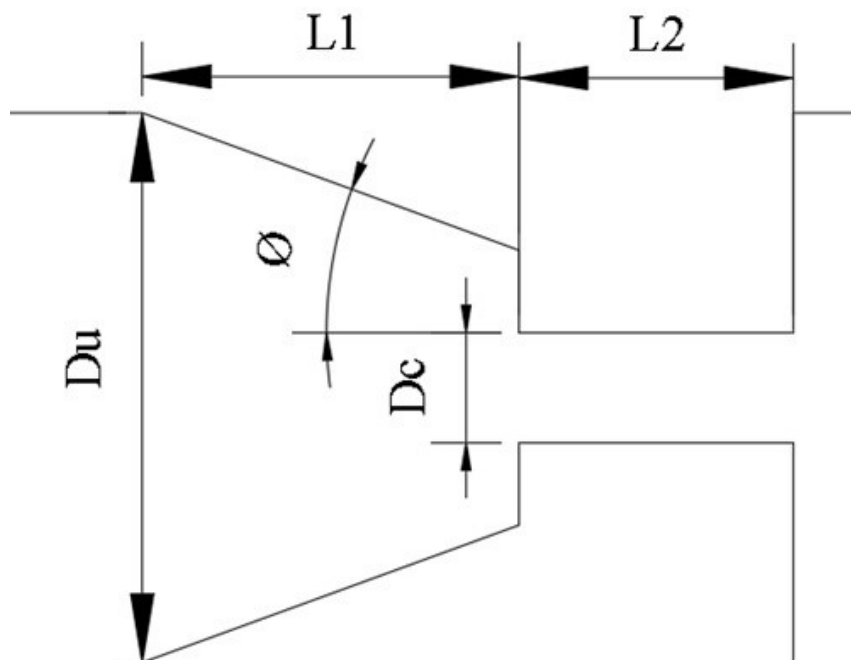


Figure 3.10: Critical dimensions of the 3D printer nozzle

Table 3.3: Important dimensions of nozzle geometry

D_u	2000 μm
D_c	400 μm
$L=L_1+L_2$	2373 μm
ϕ	20°

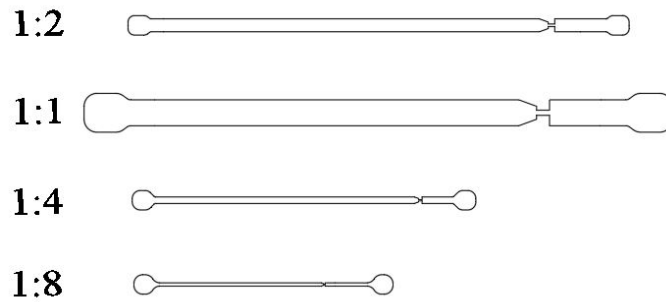


Figure 3.11: Micro-channel design with different scales

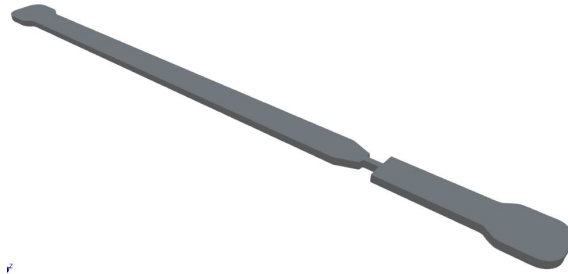


Figure 3.12: 3D sketch of a micro-channel

3.4.2 Micro-channel fabrication

From the concept and design of the micro-channel to its materialisation stands a three stage fabrication process whose details will be presented.

3.4.2.1 Pattern Mask

The first step of the process took place at Micro and Nanofabrication Unit (MNTEC) of Faculdade de Ciências da Universidade do Porto (FCUP) where the pattern mask were created. This procedure was carried out inside a clean room (ISO 14644-1) in which the concentration of airborne particles are controlled and is designed to minimize the introduction and generation of particles and microbes. The room used was classified as a class 1000, or in other designation as an ISO 6. This means that the number of particles bigger than $0.5\ \mu\text{m}$ is less than 1000.

An initial substrate consisted of chromium was spin coated with a positive photoresist, AZ1505, to ensure a uniform thickness. To guarantee a $0.5\ \mu\text{m}$ thickness the photoresist was spun at 4000 rpm during 60 seconds. After spin coating, part of the solvent is still present on the coated mask. In order to remove this solvent the substrate has to be soft baked promoting its evaporation. This soft baking was realized on a hot plate at 100°C for 60 seconds. The short time of soft baking is mainly to avoid any degradation of the photosensitivity of the compound.

To record the pattern on the soft baked substrate is was used a Heidelberg μ PG 101 direct laser writer as shown in Figure 3.13. In this process, also known as direct laser lithography, the sample is exposed to a beam of laser, in this case by a GaN laser with a 400nm wave length. The substrates are loaded on a XY stage equipped with a vacuum chuck to hold the substrate in place. The exposure power influences the amount of energy that is deposited on the surface which can be controlled by the output of the laser in mW and by setting the pixel pulse duration in percentage. In this case it was used a 3 mW, 30% energy output.



Figure 3.13: Direct writting equipment

After exposure, the chemical properties of the photoresist changed. This fact can be seen in a developer solution. The developer used was AZ726 MIF that is typically used when the photoresist is AZ1505. Since this is a positive photoresist, the exposed regions get dissolved in the developer while the unexposed regions remain on the substrate. In case of a short exposure, the energy might not be enough to activate the photo-solubilization of the resin. The post exposure substrate was submerged in the developer for 60 seconds while gently stirred. After this, the piece was washed with etanol and iso-propanol in order to remove any remnant of photoresist or developer and then submerged in Chromium etchant (Techi Etch Cr01) for a couple minutes to remove the Chromium from the substrate giving the final piece of this procedure as shown in figure 3.14.



Figure 3.14: Pattern Mask fabricated with a AZ1505 photoresist

3.4.2.2 SU-8 Mold

The second step was also achieved at Micro and Nanofabrication Unit (MNTEC) of Faculdade de Ciências da Universidade do Porto (FCUP). In this step a SU-8 was created, which will later become the master where the PDMS will be poured on.

SU-8 (glycidyl ether of bisphenol A) is an acid-catalyzed, UV photoresist based on EPON SU-8 epoxy resin. The number eight refers to the eight epoxy sites present in each monomer. SU-8 dissolved in cyclopentanone and gamma-butyrolactone solvents are classified as SU-8 2000 and SU-8 3000 series respectively. The type of series which have a characteristic viscosity, influencing the thickness of the film [64].

So to start the process was necessary to spin coat a silicon wafer with SU-8 2050 up to 3140 RPM for 30 seconds to achieve a uniform $50\text{ }\mu\text{m}$ layer. Then, the wafer was soft baked in a induction hot plate as shown in figure 3.15, first at 65°C for 2 minutes and then at 95°C for 8 minutes to ensure an adhesion to the silicon wafer and to remove the solvent, respectively.



Figure 3.15: SU-8 mold soft baked onto a hotplate

In order to transfer the patterns onto the SU-8 photoresist, the soft baked wafer undergoes a light exposure. This exposure is accomplished using a mask aligner, in this case it was used a MJB3 Mask Aligner from Karl Zuss. A mask aligner consists of three main parts, a lamp house, a microscope and a alignment stage. A typical mask aligner uses gas discharging lamps such as arc lamps. These lamps emit light in the UV and visible regions producing light ranging 365 to 440 nm. Once the pattern mask is aligned with the wafer, the light is shined as shown in figure 3.16.

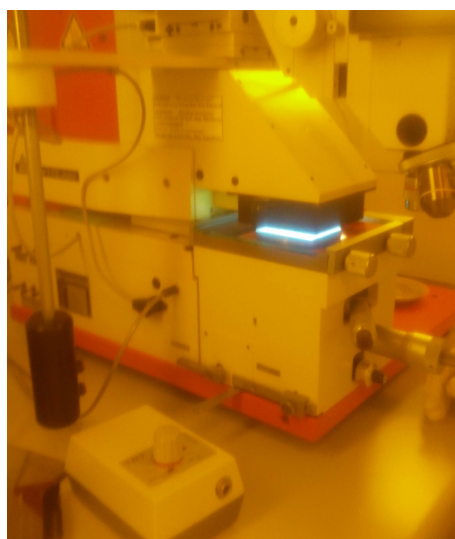


Figure 3.16: Mask aligner exposing UV light onto the SU-8

To thermally cross-link the exposed photoresist, the silicon wafer was post-baked on a hot plate, first at 65°C for 1-2 minutes and then at 95°C for 6-7 minutes and cool off at room temperature. To finish the process the post-baked wafers were developed in a SU-8 developer, PGMEA (1-methoxy-2-propanol acetate) for 6 minutes, gently stirring the mix. Since SU-8 is a negative photoresist, only the exposed parts will remain attached to the silicon substrate, all of the non-exposed areas will be washed away, resulting in a SU-8 master as shown in figure 3.17. To accelerate the

PDMS fabrication process it was fabricated 3 different SU-8 molds containing the same configuration and depth as described up to this point. The different molds were named mold A, B and C.

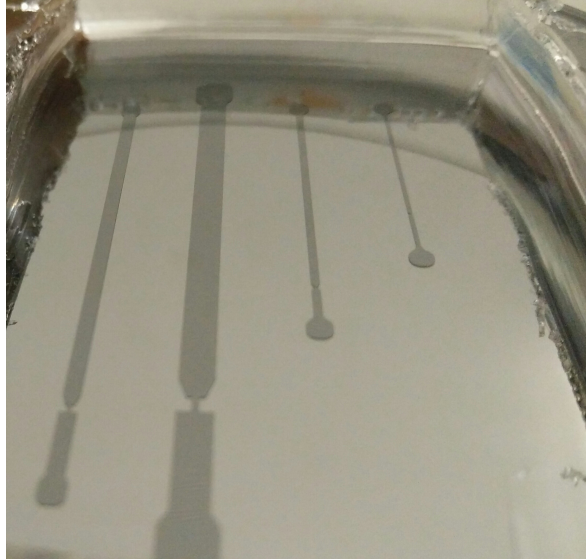


Figure 3.17: SU-8 master molds

3.4.2.3 PDMS Channels

The third and final step of the fabrication took place at Transport Phenomena Research Center of Faculdade de Engenharia da Universidade do Porto (CEFT/FEUP). Here was performed a simple soft-lithography technique using a Polydimethylsiloxane (PDMS) mixture. PDMS is a relatively cheap, soft elastomer, transparent at optically visible wavelengths. It has been used in most of microfluidics applications due to its characteristics.

The PDMS channels were fabricated using a two part Sylgard[®] 184 PDMS polymer kit (Dow Corning, Midland, MI, USA), mixed to weight ratio of 10:1 (pre-polymer : curing agent) and then mixed for 5 minutes with a spatula. This mixing process leads to the formation of air bubbles that are undesired because significantly decreases the strength of the PDMS and can create dimensional irregularities on the channels. To avoid this problem the mixture was degassed in a vacuum chamber until all the air bubbles were removed.

The SU-8 mold was prepared completing a silanization process before pouring the PDMS. Since SU-8 is quite hydrophilic, and the PDMS's affinity to silicon is very strong this would cause peeling problems when trying to demold the two parts. To avoid this problem the masks undergo a gas surface treatment with TMCS (TriMethylChloroSilane) to make it hydrophobic. Due to the toxicity of this substance the silanization was carried out under a fume hood for safety reasons as shown in figure 3.18 . It is only necessary two/three drops scattered in a plate to cause the chemical transformation. TCMS exposure lasted for about 1 hour and after this it would last up to a day without repeating the process.



Figure 3.18: Silanization process

Once this procedure was completed and PDMS free from any air bubbles, it was possible to pour the PDMS mixture onto the SU-8 mold. To avoid any air bubble the molds were placed again under vacuum and then cured in an 80°C oven for 30 minutes. The PDMS was baked to accelerate the cross-linkage process, which on its own, at room temperature, would take over 24 h to produce a solid enough result. When cured, the PDMS was gently cutted with a scalped as shown in figure 3.19 and carefully peeled off their molds.

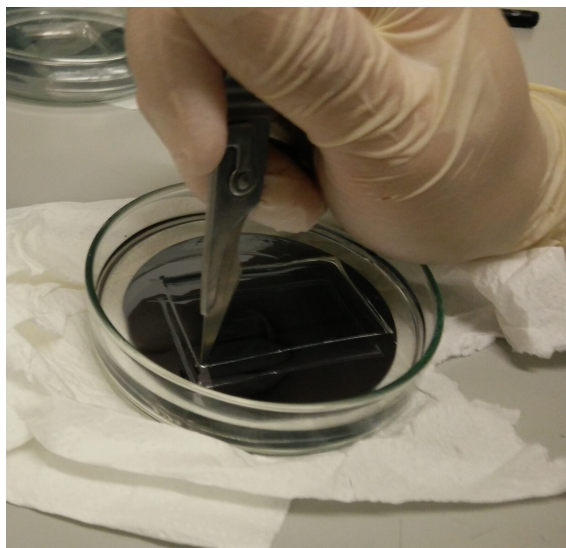


Figure 3.19: Cutting the PDMS from the SU-8 master mask

Next, the micro-channels inlet and outlet ports were made with a stainless steel tip mounted in a plastic syringe. It was used a Nordson precison tip with a inner diameter of 0.51mm and a outer diameter of 0.82mm. Finally the PDMS is ready to be bonded onto a 50x75mm microscope glass. Before any procedure, each part was cleaned to remove all dusts and particles from the surface.

To do so, the glass was submerged in Ethanol and inserted onto a ultrasonic cleaner for 8 minutes and the PDMS blown by a compressed air pistol.

To bond the PDMS to the glass was necessary to activate the surface, transforming the Si-CH₃ bonds of the PDMS into a Si-OH and then press against a surface with the same function creating a strong and permanent Si-O-Si link. The most used technique to do it is by using a plasma cleaner working with O₂ or air. Deprived of electrons, the gas molecules of the plasma react to the glass and PDMS block. Ideally, the plasma reacting to the glass and the PDMS will create on the surface silicon atoms with one missing electron. After reacting to the plasma treatment, these Silicon bonds will ideally combine with a hydrogen atom, thus creating on the PDMS and the glass surface Si-OH bonds, to replace the initial Si-CH₃ bonds. Later on, when the PDMS block comes into contact with the glass slide, these two Si-CH₃ bonds recombine to form a covalent connection Si-O-Si between the glass and the PDMS [65]. The final result can be seen in figure 3.20

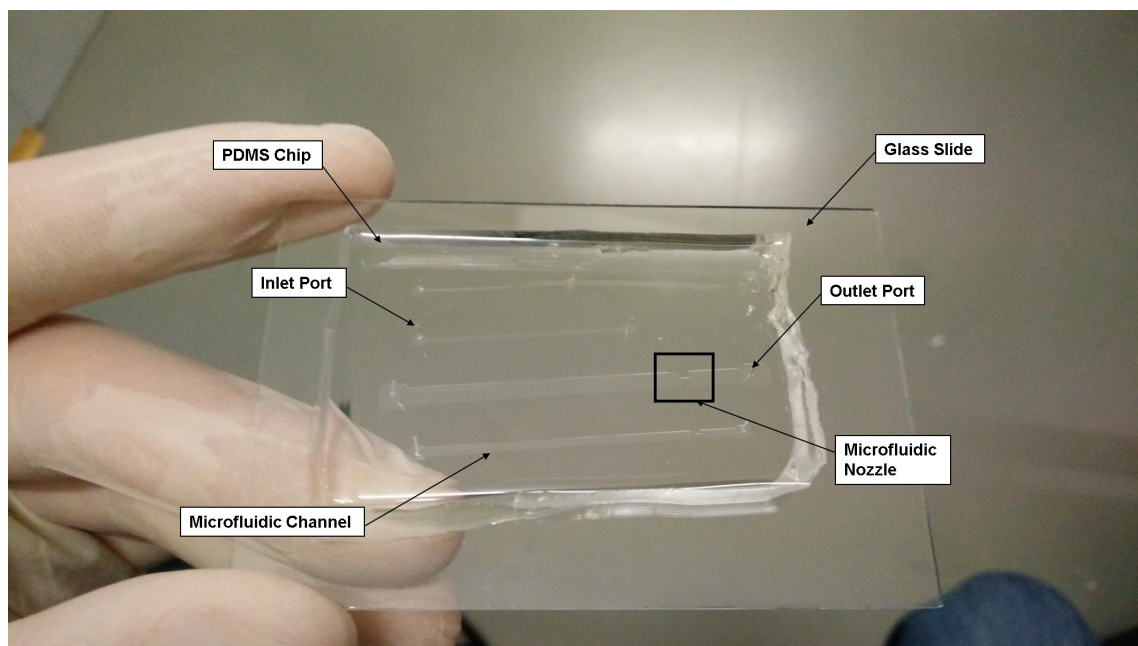


Figure 3.20: PDMS micro-channels at the end of fabrication

To guarantee that the microfluidic channels had similar distances and angles to the ones sketched in the CAD program, it was performed at CEMUP in Faculdade de Ciências da Universidade do Porto, a Scanning Electron Microscopy (SEM) images of the three micro-channels from each SU-8 mold. Figure 3.21 shows some SEM photos of the microfluidic channels and table 3.4 present the dimensions of the micro-channels. Since it is difficult to guarantee that all channels will have the exact same dimensions, the dimensions of three different PDMS micro-channels were measured, one for each SU-8 mold and then applied a Student's t-test for $p \leq 0.05$.

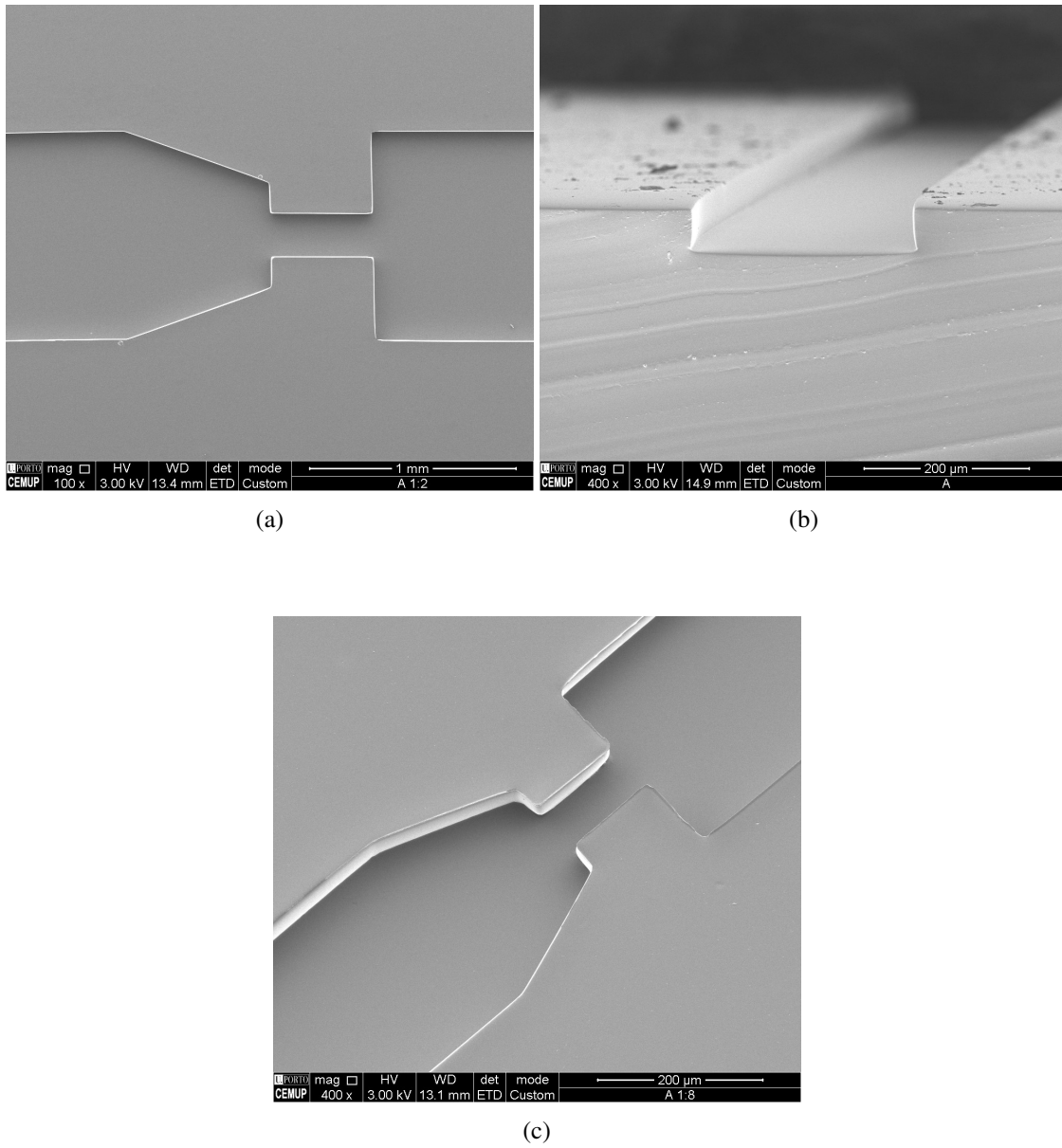


Figure 3.21: Scanning Electron Microscopy images of three types of micro-channels fabricated from high quality SU-8 photoresist moulds: a) Top view of 2D nozzle; b) View of the cross section of the micro-channel; c) Perspective image

Table 3.4: Real dimensions of the microfluidic channels taken in SEM analysis

Scale	$W_u \pm SD$	$W_c \pm SD$	$L \pm SD$	$\phi \pm SD$
1:1	2025 ± 36	401.4 ± 5.9	2396 ± 42	20.00 ± 1.10
1:2	1002 ± 14	202.5 ± 6.2	1204 ± 13	20.00 ± 1.10
1:4	504.2 ± 1.7	105.6 ± 1.6	594.6 ± 7.2	20.00 ± 1.10
1:8	255.1 ± 1.6	57.09 ± 3.24	300.9 ± 8.9	20.00 ± 1.10

3.4.3 Flow Visualization

Attending to the main objective of this work it was necessary to visualize the flow pattern along the micro-channels contraction. To achieve this goal several steps needed to be taken. First it was necessary to fill the micro-channels with the analogue fluid. To do so, a Nordson precision tip with a smaller inner diameter than the ones used to do the holes was used so that the liquid enter and exit the channels with ease, but had to be large enough to prevent leaks which could ruin the experiments. The tips used had an inner diameter of 0.33mm and an outer diameter of 0.65mm. The tips were connected via a flexible Tygon® LMT 55 tubing with a 0.44 mm inner diameter as shown in figure 3.22.

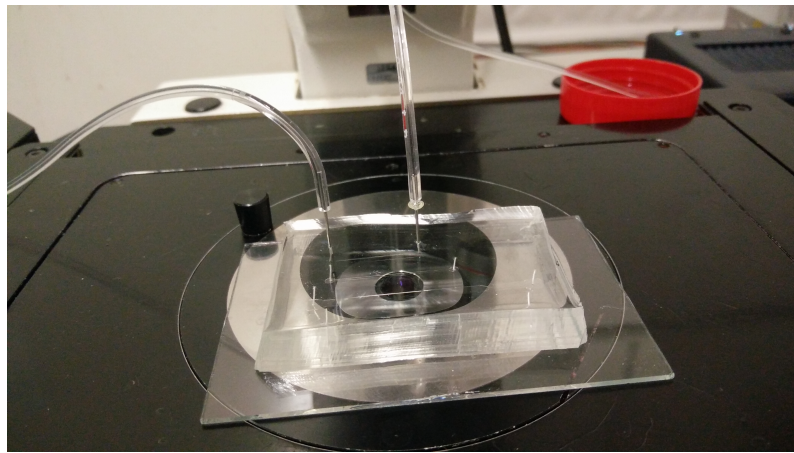


Figure 3.22: Connecting the inlet and outlet ports in PDMS with a precision tip

The outlet hole will be connected to a recipient while the inlet will be connected to a glass syringe, Hamilton 10 μ l up to 2.5ml were used depending on the required flow rate, ensuring a pulsation free inlet flow.

The flow rate was controlled by means of a neMESYS low pressure syringe pump (Cetoni GmbH 14:1). The pump operates on a motor that pushes the syringe at a constant speed. Thus to ensure that the time interval between steps on the motor is small enough not to impact the flow rate in the channels, a minimum pusher velocity must be set (hence a minimum flow rate for each syringe) below which pulsating effects might occur.

To observe the streak-lines, the analogue fluid needs to be prepared with a fluorescent micro-spheres that under a microscope fluorescent light will shine giving the perception of a streamline. The fluorescent particles used were FluoSpheres™ Carboxylate-Modified Microspheres, with a nominal bead diameter of 1 μ m submerged in a 2% solid solution. In order to guarantee a good visualization a small concentration of particles (40 and 90 ppm) were mixed in the analogue fluid and then dispersed in an ultrasonic bath for about 5 minutes.

Before any visualization it is necessary to do a surface treatment to the PDMS. PDMS presents a hydrophobic surface, mainly due to the presence of methyl groups which are hydrophobic [66].

To remove the methyl groups is necessary to perform a O_2 plasma treatment as shown in figure 3.23. The whole procedure is the same as described in section 3.4.2.3.

This procedure changes the surface of the PDMS into a more S_2O_2 like material turning this material hydrophilic. It is important to do this procedure since the fluorescent microspheres are hydrophobic and could stick to the top or bottom of the untreated PDMS micro-channels, leading to a stationary particle in the flow, inducing a very bright point on the visualization photos that could cause an interference when analysing the flow streamlines as shown in figure 3.24.



Figure 3.23: Surface treatment of PDMS in a plasma cleaner

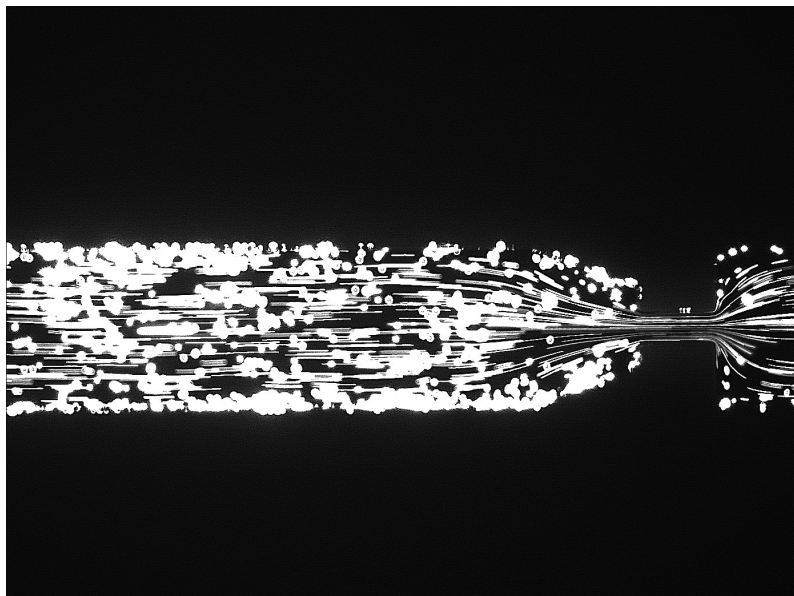


Figure 3.24: Fluorescent particles stuck at PDMS, creating very bright spots

After this procedure the micro-channels were connected to the syringe pump and placed on the imaging stage of an inverted microscope as shown in figure 3.25.

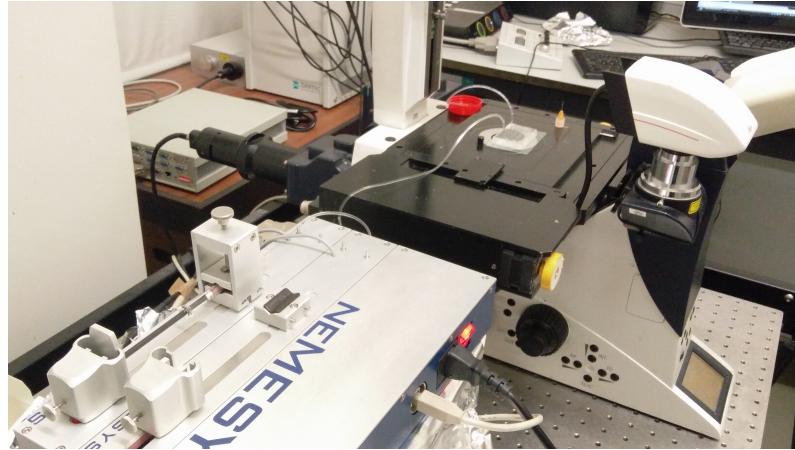


Figure 3.25: Assembly and placement of the micro-channels for flow visualizations

The microscope used was a Leica Microsystems GmbH, DMI 5000 M equipped with a sensitive monochromatic CCD camera (Leica Microsystems GmbH, DFC350 FX) and a 5,10,20 and 40x magnification objective lens (Leica HCX PL Fluotar L CORR, numerical aperture $NA = 0.40$). The microscopy images were acquired and analysed afterwards using the Leica Application Suite Software, or LAS (v3.5.0, Leica Microsystems). The microscope is also equipped with an incident fluorescent illumination (Mercury (Hg) 100 W), as shown in figure 3.26, which will be used to enhance the particles in the fluid.

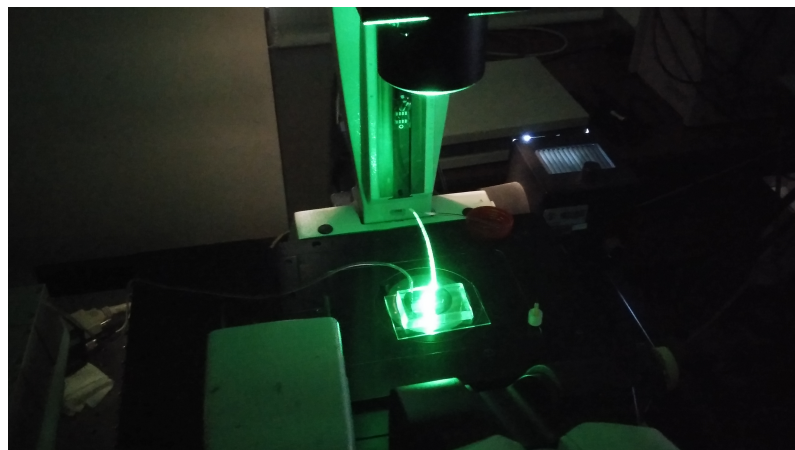


Figure 3.26: Mercury fluorescent lightning

Although the simplicity of this procedure, some precautions must be taken in account in order to produce a correct flow upstream and downstream of the contraction. There are two major problems that can occur in this type of work. The first one is related with the presence of air bubbles

inside the micro-channel that will work as an obstacle for the fluid. To eliminate this problem is necessary to wash the micro-channel with de-ionized water before inserting the analogue fluid with the fluorescent microspheres. The trapped air bubbles can escape through the PDMS since it has a good gas permeability. Another major problem can arise when PDMS debris get loose and stuck on the contraction or very close to it as shown in figure 3.27. This completely modifies the flow path around the debris and ultimately can ruin the experiment since the real flow is not verified anymore. In order to avoid this it is necessary to clean the micro-channel with compressed air after creating the inlet and outlet holes and before joining the PDMS and glass together to minimize possible debris inside the micro-channels.



Figure 3.27: PDMS debris and air bubbles trapped inside micro-channels

3.5 Dimensionless Numbers

In order to ensure a proper replication of the real flow conditions it was necessary to guarantee that the Re and De were as similar as possible to the real case. To do so, first was analysed the dimensionless numbers for the real case (prototype). At the contraction the nozzle can be seen as a cylindrical pipe so the Re takes:

$$Re_{prototype} = \frac{\rho V D}{\eta} \quad (3.41)$$

with and $Q = VA$ and $A = \frac{\pi D^2}{4}$ then

$$Re_{prototype} = \frac{4\rho Q}{\pi D_c \eta} \quad (3.42)$$

where ρ is the polymeric fluid density, Q is the flow rate, D_c the contraction diameter and η the viscosity of the melt. But is also necessary to take in account the elastic effects represented by De . In the region upstream of the contraction, the flow can be seen as a simple shear flow.

$$De_{prototype_{shear}} = \lambda \dot{\gamma} \quad (3.43)$$

where $\dot{\gamma} \approx \frac{\bar{V}_c}{D_c/2}$, so the previous equation can be re written as:

$$De_{prototype_{shear}} = \lambda \frac{\bar{V}_c}{D_c/2} \quad (3.44)$$

with $Q=VA$, then

$$De_{prototype_{shear}} = \frac{8\lambda Q}{\pi D_c^3} \quad (3.45)$$

However at the centreline of the contraction-expansion, the flow is similar to a purely extensional one and essentially shear-free [67]. If we consider a strain rate that assumes a velocity as the one in the contraction centreline where it takes its maximum value then the equation we have:

$$De_{prototype_{extensional}} = \lambda \dot{\epsilon} \quad (3.46)$$

where:

$$\dot{\epsilon} \approx \frac{\delta V_x}{\delta x} \approx \frac{V_c - V_u}{L} \quad (3.47)$$

where V_c is the maximum velocity at the contraction, V_u is the maximum velocity upstream of the contraction and $L=L_1+L_2$ (figure 3.10). The maximum velocity can be related to the average velocity with a coefficient k as:

$$V_{max} = k\bar{V} \quad (3.48)$$

Then the strain rate at the centreline can be calculated as [68]:

$$\dot{\epsilon} = \left(k_c \frac{4Q}{\pi D_c^2} - k_u \frac{4Q}{\pi D_u^2} \right) / L \quad (3.49)$$

where D_u is the diameter upstream, D_c is the diameter of the contraction and k_u and k_c is only a function of the scale and can be calculated as shown by Deplace et.al [69] by:

$$k = \frac{v_{max}}{\bar{v}} = \frac{\pi^4}{64 \sum_{n=1,3,5,\dots}^{\infty} \frac{1}{n^4} \left(1 - \frac{2a}{n\pi b} \tanh\left(\frac{n\pi b}{2a}\right)\right)} - \frac{\pi \sum_{n=1,3,5,\dots}^{\infty} \frac{1}{n^3} (-1)^{\frac{n-1}{2}} \frac{1}{\cosh\left(\frac{n\pi b}{2a}\right)}}{2 \sum_{n=1,3,5,\dots}^{\infty} \frac{1}{n^4} \left(1 - \frac{2a}{n\pi b} \tanh\left(\frac{n\pi b}{2a}\right)\right)} \quad (3.50)$$

where b is the width and a the depth of the channel. For pipes of circular cross-section, which is the case of the 3D printing nozzle, $k=2$. So using the maximum velocity methodology, De can be written as:

$$De_{prototype_{extensional}} = \frac{8\lambda Q}{\pi L} \left(\frac{1}{D_c^2} - \frac{1}{D_u^2} \right) \quad (3.51)$$

In the case of the micro-channels the cross section is a rectangular one, so Re needs to incorporate this geometrical shape. It can be defined as:

$$Re_{channel} = \frac{\rho V D_h}{\eta} \quad (3.52)$$

with D_h representing the hydraulic diameter of the micro-channel which can be seen as:

$$D_h = \frac{4A}{P} \quad (3.53)$$

where A is the area and P the perimeter of the rectangular cross-section. Assuming w_c as the contraction width and h as depth of the micro-channel then D_h can be written as:

$$D_h = \frac{2w_ch}{w_c + h} \quad (3.54)$$

replacing equation 3.54 into equation 3.52, Re number inside the micro-channel takes:

$$Re_{model} = \frac{2\rho Q}{(w_c + h)\eta} \quad (3.55)$$

also De changes due to the rectangular shape of the channels. For the shear definition it takes:

$$De_{model_{shear}} = \lambda \dot{\gamma} \quad (3.56)$$

bearing in mind that now $A = w_ch$

$$De_{model_{shear}} = \frac{2\lambda Q}{hw_c^2} \quad (3.57)$$

where w_c is the contraction width and w_u the upstream width. For the maximum velocity criteria, is introduced a modification on equation 3.51 mainly the value of the k coefficients discussed previously. The De number considering the maximum velocity comes as:

$$De_{model_{extensional}} = \frac{\lambda Q}{hL} \left(\frac{k_c}{w_c} - \frac{k_u}{w_u} \right) \quad (3.58)$$

Since we have two possible expressions to calculate De , it is necessary to establish a criteria to choose one of them. If we analyse the shear expression (equations 3.45 and 3.57) in both prototype and micro-channel geometry we see that the only geometrical parameter present is the contraction diameter or width, respectively. With this approach it is not considered the upstream diameter/width neither the length of it, so we are missing information about the contraction-expansion effect. By considering the maximum velocity criteria (equations 3.51 and 3.58), all the geometrical parameters are present, and so it is possible to describe more accurately the flow inside the nozzle. So the extensional approach is the one that will be used in this work.

Finally, since all of the channels were produced with the same depth but with different scales, the width/depth ratio will change from each set of scales, taking the values presented in table 3.5.

Table 3.5: Width/Depth ratio between each set of micro-channels

Scales	w_u/h	w_c/h
1:1	40	8
1:2	20	4
1:4	10	2
1:8	5	1

3.6 Uncertainty analysis

A careful analysis of the experimental uncertainty in this study is critical to the interpretation of the experimental data and exploration of deviations from the theory. Experimental uncertainties were estimated for Re, De and El.

The uncertainty associated with Re, is based on the actual dimensions of the micro-channels cross-section, w_c (width at the contraction) and h (depth). Also it was considered a uncertainty the measurement of density (ρ). The uncertainty can be estimated by using:

$$\delta Re = \left[\left(\frac{\delta Re}{\delta \eta} \delta \eta \right)^2 + \left(\frac{\delta Re}{\delta Q} \delta Q \right)^2 + \left(\frac{\delta Re}{\delta \rho} \delta \rho \right)^2 + \left(\frac{\delta Re}{\delta w_c} \delta w_c \right)^2 + \left(\frac{\delta Re}{\delta h} \delta h \right)^2 \right]^{1/2} \quad (3.59)$$

where δw_c , δh , $\delta \rho$ are the uncertainties in the average values of the width and depth, respectively, measured in the actual micro-channels and in the calculated density value.

For the De it is also necessary to take in consideration the uncertainty with measuring the length of the contraction area (L), the width on the upstream area (w_u) and with the determination of the relaxation time (λ) resulting in:

$$\delta De = \left[\left(\frac{\delta De}{\delta Q} \delta Q \right)^2 + \left(\frac{\delta De}{\delta \lambda} \delta \lambda \right)^2 + \left(\frac{\delta De}{\delta w_u} \delta w_u \right)^2 + \left(\frac{\delta De}{\delta w_c} \delta w_c \right)^2 + \left(\frac{\delta De}{\delta h} \delta h \right)^2 + \left(\frac{\delta De}{\delta L} \delta L \right)^2 \right]^{1/2} \quad (3.60)$$

where δw_u , δL , $\delta \lambda$ are the uncertainties in the average values of the upstream width, length of contraction area and relaxation time, respectively.

Finally the El number results in a combination of De with Re number so the uncertainty takes:

$$\delta El = \left[\left(\frac{\delta El}{\delta Re} \delta Re \right)^2 + \left(\frac{\delta El}{\delta De} \delta De \right)^2 \right]^{1/2} \quad (3.61)$$

All uncertainties were calculated using Engineering Equation Solver (EES) and its Uncertainty Propagation Tool.

Chapter 4

Results and Discussion

4.1 Polycarbonate

To perform this study it was necessary to establish a benchmark in order to correctly replicate the flow conditions on the microfluidic devices. This benchmark was of course defined by the real conditions occurring during a printing process. So to evaluate the dimensionless numbers described in section 3.5 it was necessary to determine the unknown properties of the polycarbonate, namely its viscosity (η) and its relaxation time (λ). In order to collect these values it was used, as referred in section 3.1 the book, "Handbook of Polycarbonate Science and Technology" [51] to obtain the master curves for η and G' and G'' as shown in figure 4.1.

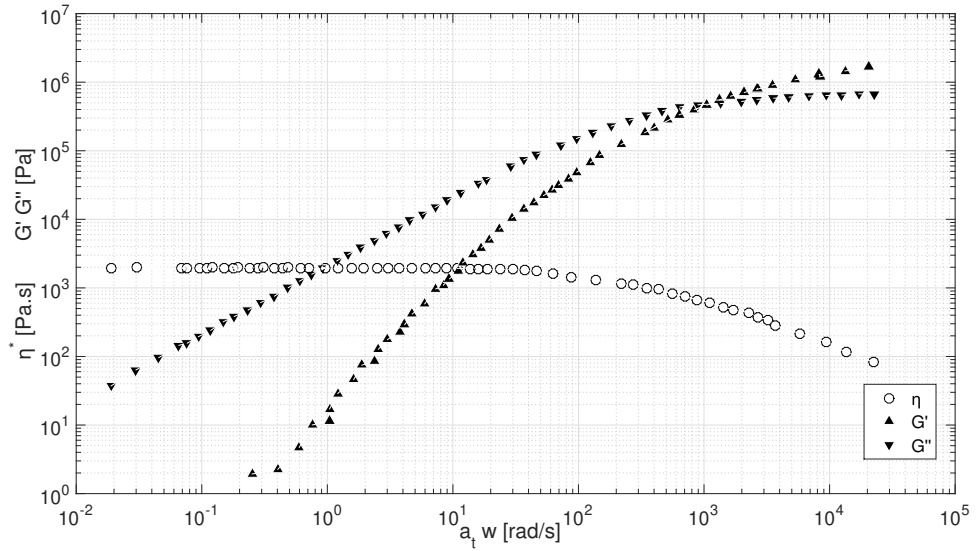


Figure 4.1: Master curve of dynamic properties of PC54: reference temperature of 275°C [51]

However the viscosity in figure 4.1 is a complex viscosity (η^*). Nevertheless, for polymeric flows, the complex and shear viscosity have the same magnitude, as suggested by the Cox-Merz

rule. This rule is generally very important when only the linear viscoelastic data are available [30].

$$\eta(\dot{\gamma}) = |\eta^*(\omega)| \quad (4.1)$$

Since this polycarbonate has a shear thinning behaviour at higher shear rates its imperial to determine the shear rate at the nozzle since it can affect this parameter and influence the Re and De calculation. If we use the definition of shear rate for a Newtonian fluid through a pipe we take:

$$\dot{\gamma} = \frac{\bar{V}_c}{D_c/2} \quad (4.2)$$

taking $Q = \bar{V}_c A$ thus:

$$\dot{\gamma} = \frac{2Q}{\pi \frac{D_c^3}{4}} \quad (4.3)$$

so:

$$\dot{\gamma} = \frac{8Q}{\pi D_c^3} \quad (4.4)$$

where $\dot{\gamma}$ units are $1/s$; Q is the flow rate and D_c is the contraction diameter of the nozzle. The flow rate is a printing parameter and for this study will be consider a range between 10 and 50 mm^3/s . Each flow rate will produce a different shear rate at the contraction which will give different value of viscosity and ultimately a different Re. The shear rate values were then converted to rad/s since [70]:

$$\omega = 2\pi f_c \quad (4.5)$$

where ω is expressed in rad/s and f_c is expressed in Hz which is $1/s$. Table 4.1 displays the shear rate that enabled a direct read in the graph of figure 4.1. It was possible to perform a straight read from the figure since it was considered a printing temperature of $275^\circ C$ that it is inside of the printing range described section 3.1. If any other temperature were to be considered it would be necessary to introduce a shift scale a_t in order to perform a correct read of the graph.

Table 4.1: Viscosity depending on flow rate and shear rate

$Q [mm^3/s]$	$\dot{\gamma} [1/s]$	$\omega [rad/s]$	$\eta [Pa.s]$
10	397.9	2500	502.3
20	795.8	5000	306.2
30	1194	7500	214.0
40	1592	1.000×10^4	171.2
50	1989	1.250×10^4	147.3

The relaxation time was obtained by the crossing of G'' and G' as explained in section 3.3.2 since this technique would give a good approximation when missing a proper extensional characterization of the molten polymer. The crossing frequency is given in rad/s however is necessary to convert it to 1/s, as shown in table 4.2, in order to obtain a correct value of the relaxation time.

The last parameter necessary to calculate the dimensionless numbers is the density of the molten polymer at the considered temperature which can be expressed as shown in equation 4.6 [71].

$$\rho = \frac{10^3}{\exp(-0.307 + 1.86 \times 10^{-5} T^{3/2})} \quad (4.6)$$

Table 4.2: Crossing frequency and relaxation time of PC54

$\omega_{crossing}$ [rad/s]	1146.6
$\dot{\gamma}_{crossing}$ [1/s]	182.48
Relaxation time (λ) [s]	5.48×10^{-3}
Density (ρ) [kg/m^3]	1070.7

Finally it was possible to calculate Re and De (equations 3.42 and 3.51) for the real case as shown in chapter 3.4.2.3 for each flow rate given the following values expressed in table 4.3.

Table 4.3: Dimensionless numbers for the 3D printing nozzle printing a PC54 polymer

Q [mm^3/s]	Re	De	El
10	6.79×10^{-5}	0.322	4.74×10^3
20	2.18×10^{-4}	0.644	2.89×10^3
30	4.78×10^{-4}	0.966	2.02×10^3
40	7.79×10^{-4}	1.29	1.62×10^3
50	1.16×10^{-3}	1.61	1.39×10^3

It is interesting to note that although El does not depend directly on the flow rate, its value can almost double or been cut in half depending on each flow condition. This can be explained by the variation of viscosity due to the shear-thinning behaviour of the molten polymer. As the velocity of printing decreases the viscosity increase substantially lowering Re to the point that is a bigger decrease than De promoting a higher El, in other words, enhancing the elastic effects and lowering the inertial ones. Based on this, it was decided to analyse the flow pattern inside the nozzle at different El numbers since it can correspond to different printing speeds.

4.2 Analogue fluids

To replicate the behaviour exhibited by the polycarbonate it was necessary to perform a rheological analysis of the prepared analogue fluids to verify if the same EI could be achieved in order to reach our objective of replicating the printing conditions. First it was necessary to collect the viscosity curves of the different fluids as shown in figures 4.2 and 4.3.

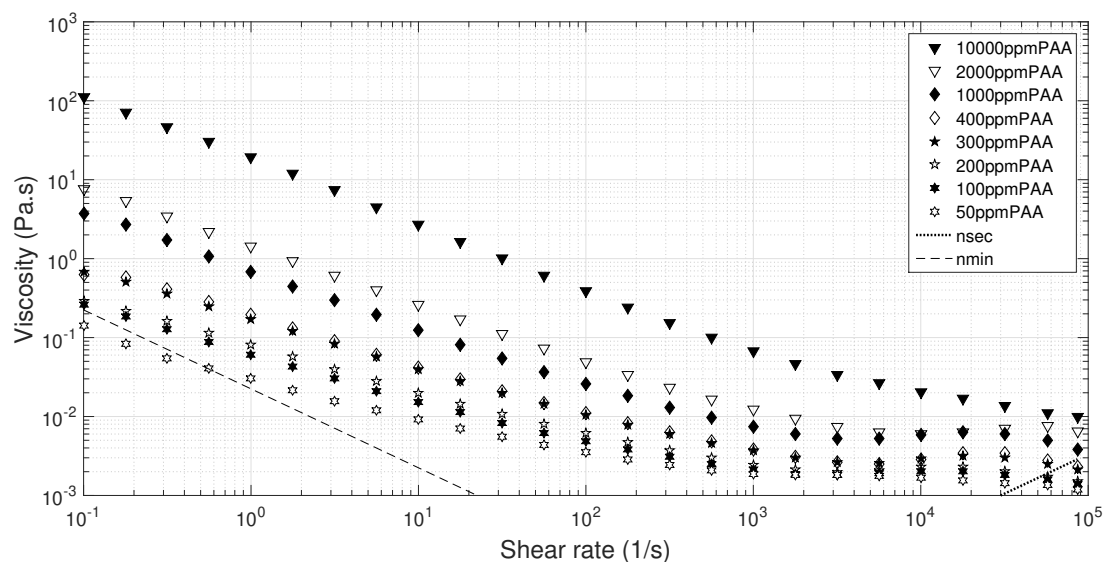


Figure 4.2: Viscosity curves for type A samples

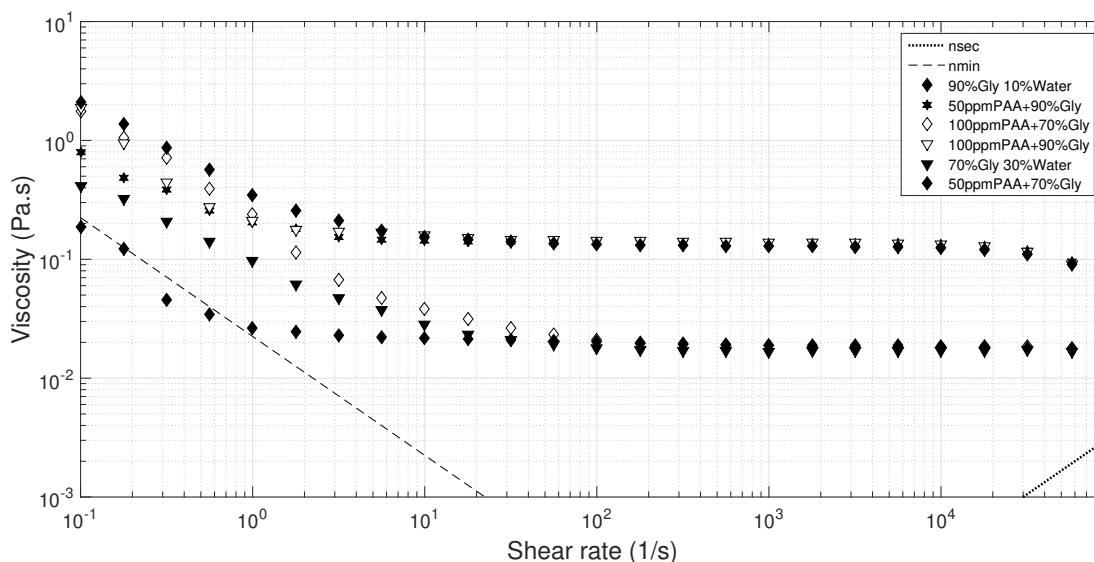


Figure 4.3: Viscosity curves for type B and type C samples

In order to determine the relaxation time of the samples at first it was decided to replicate the method used to determine the polycarbonate time. However if we analyse the G' and G'' curves of

the lower concentration samples as shown in figure 4.4 it is not clear that these two lines intercept which makes it impossible to determine the relaxation time by this method, due to a strong decay of G' at around 10 rad/s since some data are below the instrument inertia limit and this fact could be preventing us from getting a interception.

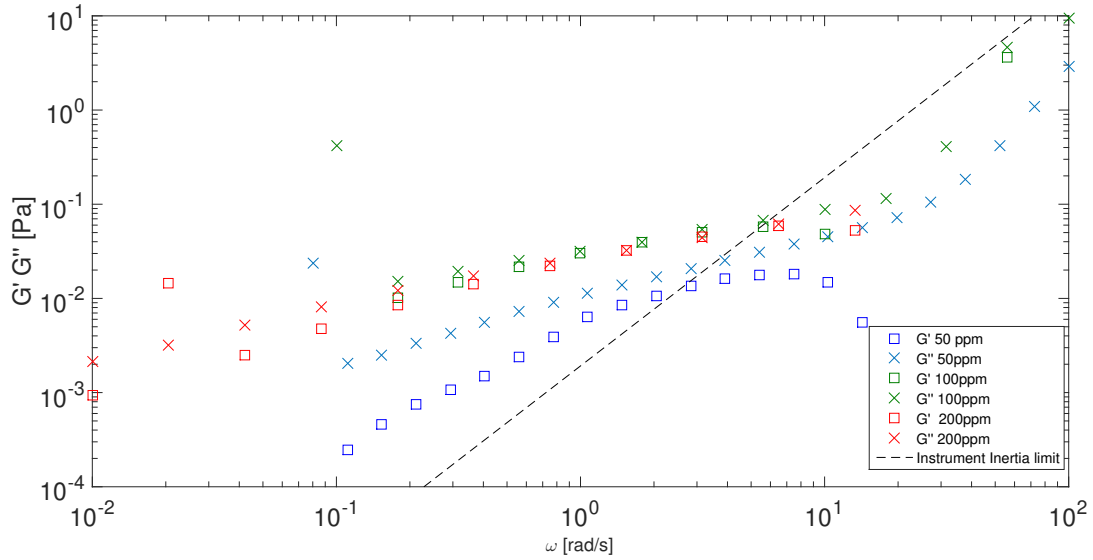


Figure 4.4: G' G'' curves of 50,100 and 200 ppm PAA samples

As an alternative it was decided to perform an extensional rheometry on the samples in order to determine its relaxation time.

To reduce the amount of experiments in extensional rheometry it was performed a first dimensionless analysis of the samples with the available data. For the samples up to 400ppm PAA in water it was used the extensional relaxation times presented in the work of C. Sousa et.al. [72] as an first approximation to see if they could be a good possibility to characterize our problem. In this work it is stated that the relaxation time of PAA in an aqueous solution can be approximated by:

$$\lambda = 0.045c^{1.14} \quad (4.7)$$

where λ is the relaxation time in milliseconds [ms] and c the concentration of PAA in parts per million [ppm].

Table 4.4 gives the necessary properties to calculate Re and De . The viscosity was considered the one that corresponds to a shear rate of 1 [1/s] since it represents a trustable value that could be extracted from the rheometer, well inside its maximum resolution range and at the same time would work as an upper limit, in other words, it represents the maximum viscosity value for that fluid in order to increase El as far as possible. Finally, the density of the samples were considered the same as water at 20°C.

Table 4.4: Viscosity, relaxation time and density of PAA samples

PAA Sample	η [Pa.s]	λ [ms]	ρ [kg/m ³]
50 ppm	0.03042	3.891	998.2
100 ppm	0.06071	8.575	998.2
200 ppm	0.08088	18.90	998.2
300 ppm	0.1727	30.00	998.2
400 ppm	0.1919	41.64	998.2

With these properties defined is possible to calculate El, via a relation between Re and De that are defined in equations 3.55 and 3.58 respectively. So it possible to determine El for each micro-channel as shown in table 4.5.

Table 4.5: Elasticity number for lower concentration PAA samples in different scales channels

PAA sample	El			
	1:1 channel	1:2 channel	1:4 channel	1:8 channel
50 ppm	0.6897	1.688	4.625	12.16
100 ppm	3.035	7.428	20.35	53.53
200 ppm	8.915	21.82	59.80	157.2
300 ppm	30.21	73.94	202.6	532.8
400 ppm	46.59	114.0	312.4	821.7

The lower concentration PAA samples show that its El is too low when compared with the polycarbonate, in fact only the 400ppm PAA in 1:8 channel scale could give a flow condition relatively closer to the 50 mm³/s flow rate of the polycarbonate. If we compare Re and De of these two situations, as shown in table 4.6, they are several orders of magnitude smaller from each other. To compensate this fact it might be reasonable to think its just a matter of increasing the flow rate in order to increase their value, however this would increase the shear rate at the contraction which due to the shear thinning behaviour of the PAA samples will lower the viscosity which ultimately would lead to a decrease in El which its not desired.

Table 4.6: Comparison between the PC and 400ppm dimensionless numbers

	Re	De	El
400 ppm 1:8 channel	8.25×10^{-6}	0.00678	8.21×10^2
PC 50mm³/s	1.16×10^{-3}	1.61	1.39×10^3

In spite of these not so good El numbers, it opens a good perspective for higher concentrations, so the 1000, 2000 and 10000ppm were analysed in extensional rheometry as there is a lack of references of the values of these relaxation times in the literature for these polymer concentrations.

The B and C type were also discarded since some of these type of fluids did not exhibit the shear thinning behaviour that the polycarbonate does and the ones who did, could not replicate the printing conditions. This is an important characteristic to replicate since it can be responsible for the backflow problems in a 3D printer [9].

To analyse the remaining samples it was performed an extensional rheometry in a CaBER 1TM, where filament thinning process was recorded using a high speed video camera (Photron FASTCAM Mini UX100). Each experiment was repeated for each sample 5 times to guarantee a good reproducibility of the results. The relaxation time of each sample are presented in table 4.7.

Table 4.7: Relaxation time for 1000,2000 and 10000ppm PAA samples

PAA Sample	λ [s]
1000ppm	0.139 ± 0.003
2000ppm	0.135 ± 0.005
10000ppm	1.57 ± 0.16

The 2000ppm PAA sample exhibits a similar relaxation time than the lower concentrated 1000ppm PAA, which is not a logical result. When we compare the results with the ones given by equation 4.7 it becomes clear that the 2000ppm sample is not obtaining credible results. In order to obtain a coherent outcome, the 2000ppm will not be used for the flow visualizations. A possible explication for this fact may reside in the mixing process, as the magnetic stirrers could have been spinning too fast and degraded the polymer chains resulting in a less viscosity and relaxation time [73].

On the other hand the 1000 and 10000ppm samples have relaxation times inside of the expected range which qualifies these fluids to be used for the flow path visualizations but first is necessary to confirm the dimensionless numbers in order to choose in which conditions they would replicate the printing conditions. To do so it was set PC with a flow rate of $30 \text{ mm}^3/\text{s}$ as a benchmark since this is an intermediate flow rate and would give a solid indication if the fluids could achieve this condition and if is possible to accurately replicate Re and De .

First, it is necessary to calculate two parameters presented in section 3.5 that have not been discussed yet. One of these parameters is the k 's coefficients present in equation 3.50 with the parameters a and b adapted for each channel with different scales. The values for k coefficient upstream of the contraction and at the contraction are present in table 4.8.

Table 4.8: K coefficients for each microfluidic channel

Ratio	Ku	Kc
1:1	1.524	1.628
1:2	1.549	1.773
1:4	1.601	1.992
1:8	1.715	2.096

The other parameter necessary is the density of the PAA in water samples. Since a small amount of sample was prepared for each analogue it was not possible to experimentally determine the density of each sample. As an alternative it was used an equation present in the work of Saravanan et.al. [74] where the density can be expressed by the equation:

$$\rho = A + B_1w + B_2w^2 + B_3w^3 \quad (4.8)$$

where ρ is density of the solution at the desired temperature; A, B_1, B_2, B_3 are coefficients of the polynomial that varies with temperature and w is mass fraction of PAA in the solution. The density was calculated for a temperature of 20°C as presented in table 4.9.

Table 4.9: Density for PAA+water samples at 20°C

PAA sample	w	A	B_1	B_2	B_3	ρ [g/cm ³]
1000 ppm	0.001	0.9982	0.3196	0.1435	-0.1493	998.5 ± 20.0
10000 ppm	0.01					1001 ± 20.0

Finally to calculate the dimensionless numbers is necessary to determine the shear at the microfluidic contraction. Adapting equation 4.2 with $A=hw_c$.

$$\dot{\gamma} = \frac{2Q}{w_c^2 h} \quad (4.9)$$

The dimensionless numbers for 1000 ppm and 10000 ppm of PAA in water that pretend to simulate one of the printing conditions are presented in table 4.10 and 4.11 respectively.

Table 4.10: Dimensionless numbers for 1000 ppm PAA sample

Scale	$\dot{\gamma}$ [1/s]	Re	De	El
1:1	0.3474	2.858×10^{-6}	5.350×10^{-3}	1873
1:2	0.5806	4.905×10^{-6}	9.875×10^{-3}	2013
1:4	2.253	1.903×10^{-5}	0.04141	2176
1:8	8.475	7.538×10^{-5}	0.1672	2218

Table 4.11: Dimensionless numbers for 10000 ppm PAA sample

Scale	$\dot{\gamma}$ [1/s]	Re	De	El
1:1	218.1	0.01824	35.01	1920
1:2	603.3	0.05720	116.5	2021
1:4	2158	0.3209	692.4	2158
1:8	1.107×10^4	1.280	2828	2209

It is important to note that for the 1000 PAA samples in the channels with scales of 1:1 and 1:2 it is possible to achieve the El desired but the shear rate at the contraction is lower than 1 [1/s] which is a zone of the rheometer where it could have a greater dispersion between measurements, so some care must be taken when collecting data from this area.

As can be seen in table 4.10 and 4.11 it is possible to achieve the same El in any of the micro-channels, however it is not possible to exactly replicate both Re and De of the polycarbonate at the same time which makes it impossible to fully replicate the printing conditions.

But if we analyse more carefully both tables, it is possible to see that we have a list of points around the same printing condition which potentiates the creation of a De-Re flow pattern map in order to collect a full picture of the possible flow conditions, as shown in figure 4.5. So it was chosen 6 values of El that could represent 6 different printing conditions. Inside each El will be chosen 4 points, 2 of them at lower Re and De and 2 at higher Re and De in an attempt to represent all the different flow conditions possible. With this configuration it would be easier to predict the behaviour inside the FDM printer and give an idea of the perfect flow condition for this geometrical configuration.

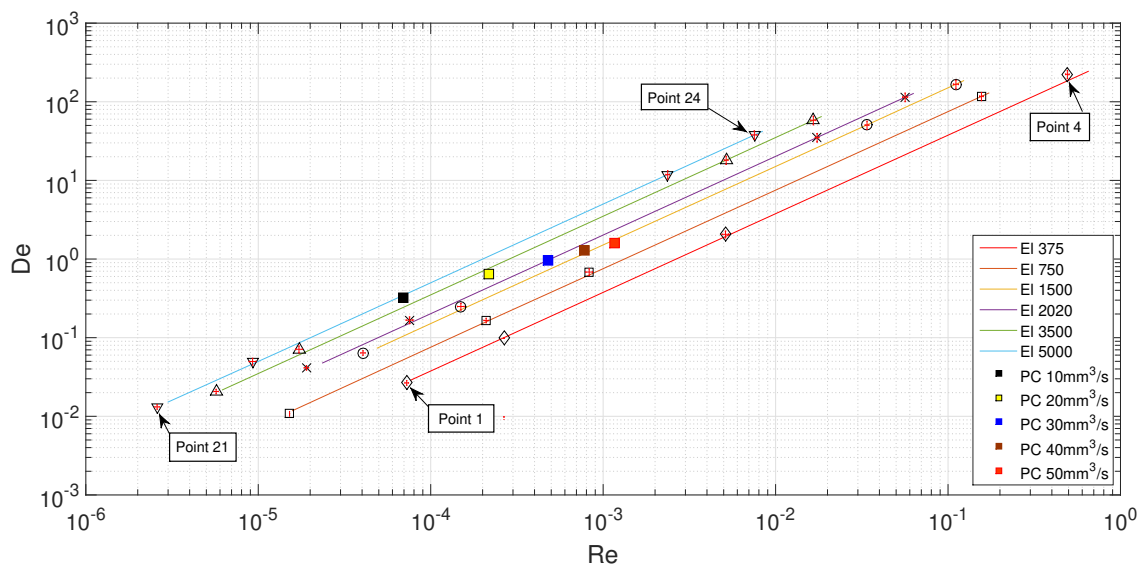


Figure 4.5: De-Re flow map

The points selected were then chosen and represented as dots in figure 4.5 with Re, De and El presented in table 4.12 with the respective uncertainty. The square points represent different printing conditions that are actually used.

Table 4.12: Dimensionless numbers of several printing conditions and of the various testing points

	$(Re \pm SD) \times 10^3$	$De \pm SD$	$El \pm SD$
PC 10 mm^3/s	0.06789	0.3219	4643
PC 20 mm^3/s	0.2185	0.6439	2955
PC 30 mm^3/s	0.4778	0.9658	2021
PC 40 mm^3/s	0.7791	1.288	1653
PC 50 mm^3/s	1.159	1.610	1389
Point 1	0.0724 ± 0.0180	0.027 ± 0.002	366.9 ± 22.7
Point 2	0.2671 ± 0.0090	0.098 ± 0.007	368.0 ± 21.1
Point 3	5.125 ± 0.229	2.063 ± 0.201	402.6 ± 26.5
Point 4	493.7 ± 12.20	223.4 ± 26.7	452.6 ± 53.0
Point 5	0.01515 ± 0.0038	0.011 ± 0.001	714.2 ± 44.1
Point 6	0.2097 ± 0.0062	0.1656 ± 0.0108	789.8 ± 40.4
Point 7	0.8301 ± 0.0371	0.6831 ± 0.0664	822.9 ± 54.2
Point 8	156.50 ± 3.9000	117.3 ± 14.0	749.4 ± 87.7
Point 9	0.04262 ± 0.0012	0.066 ± 0.004	1545 ± 79
Point 10	0.1496 ± 0.0067	0.2490 ± 0.0242	1664 ± 110
Point 11	33.980 ± 0.840	50.50 ± 6.04	1486 ± 174
Point 12	111.2 ± 3.7	166.9 ± 20.5	1501 ± 172
Point 13	0.0190 ± 0.0006	0.041 ± 0.003	2176 ± 111
Point 14	0.0754 ± 0.0034	0.1672 ± 0.0163	2218 ± 146
Point 15	17.460 ± 0.4300	35.10 ± 4.19	2008 ± 236
Point 16	56.560 ± 1.9000	114.5 ± 14.1	2025 ± 232
Point 17	0.0048 ± 0.0001	0.019 ± 0.001	3900 ± 199
Point 18	0.0172 ± 0.0008	0.007 ± 0.001	4132 ± 272
Point 19	5.1830 ± 0.1290	18.10 ± 2.16	3491 ± 409
Point 20	16.580 ± 0.5600	58.20 ± 7.17	3511 ± 403
Point 21	0.0026 ± 0.00008	0.00013 ± 0.00009	5084 ± 260
Point 22	0.0093 ± 0.00041	0.0050 ± 0.0005	5372 ± 353
Point 23	23.740 ± 0.5800	11.84 ± 1.42	4987 ± 584
Point 24	7.5490 ± 0.2530	37.90 ± 4.66	5014 ± 575

By combining different scale geometries with different flow rates it is possible to achieve all of these points maintaining a coherent and progressive outcome.

First it was performed an experiment with De-ionized water. Since it is a Newtonian fluid flow it is expected to exhibit a laminar profile at low Re . Above a critical Re the flow transforms into an asymmetric flow pattern with generation of vortices downstream of the contraction as shown in the works of Campo-Deaño et.al [14].

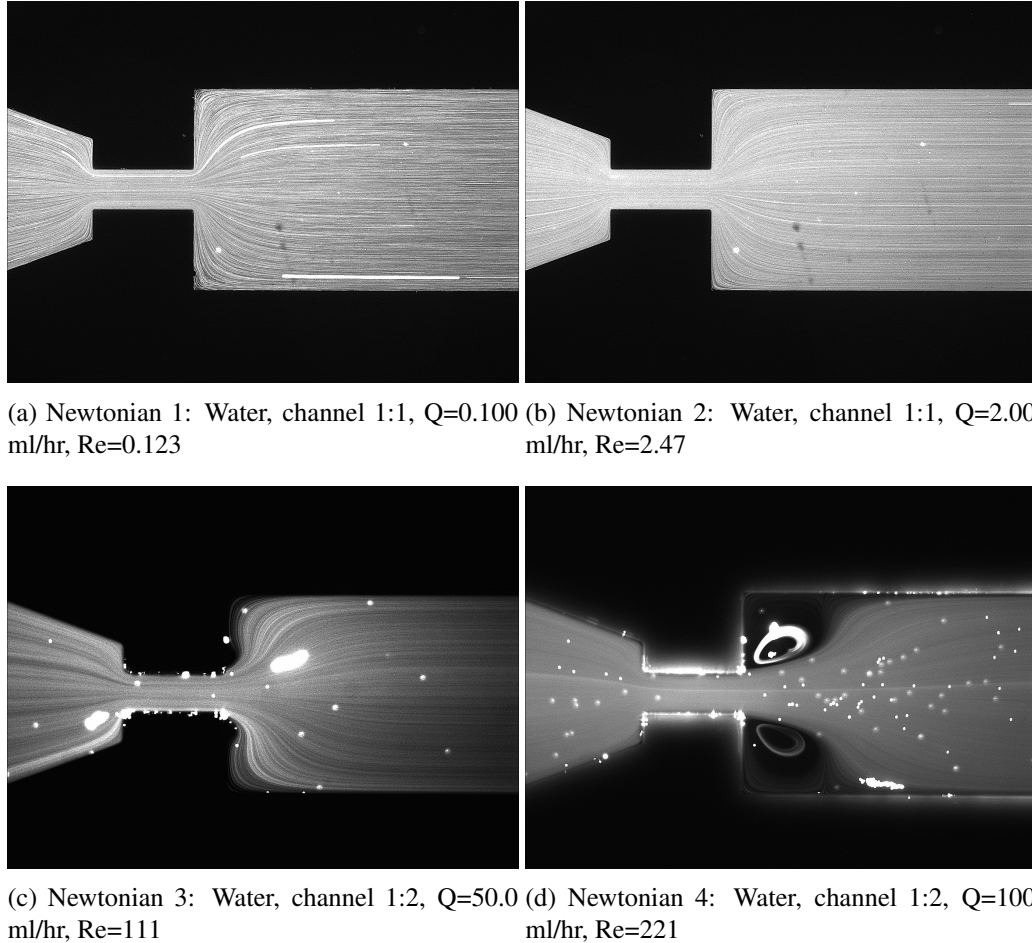
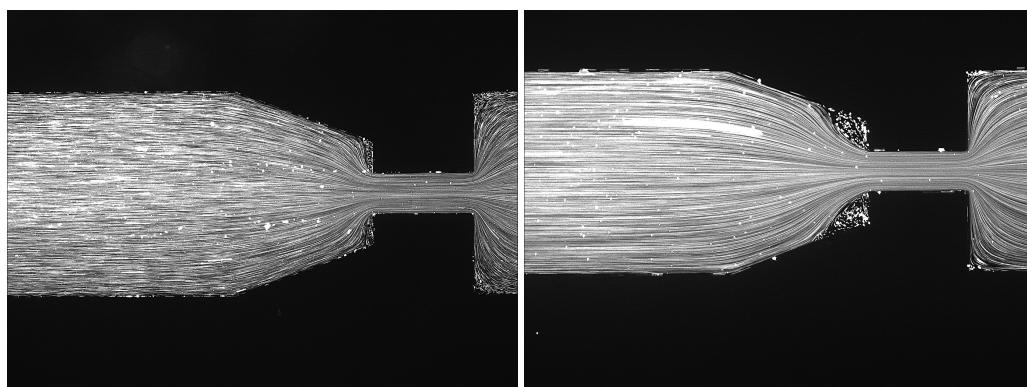


Figure 4.6: Flow pattern for a Newtonian fluid at different flow rates. The flow direction is from left to right

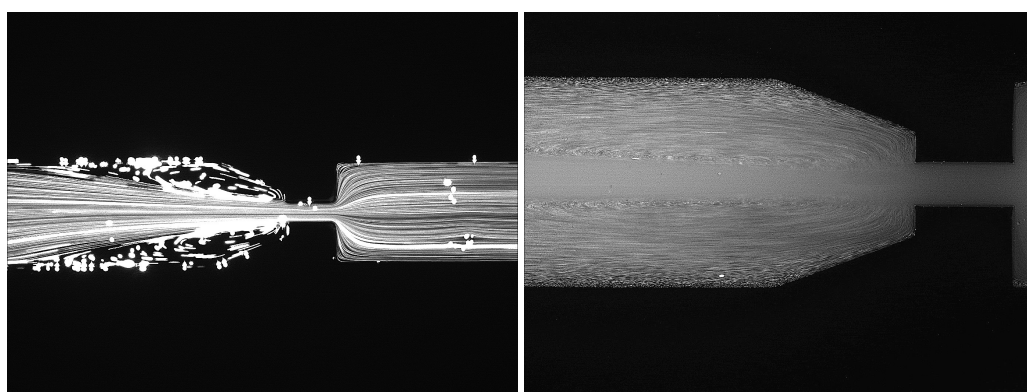
As predicted after a critical Re the effects of the expansion are felt downstream, creating and developing vortices right after the sudden expansion. This phenomena occurs due to an inefficient dissipation of kinetic energy as the the fluid decelerates as it pass to the expansion area, creating a recirculation zone due to a pressure loss [68].

For the PAA samples, since they are non-Newtonian fluids is expected symmetric vortices development upstream of the contraction which is an absolute opposite behaviour when comparing with Newtonian fluids due to the presence of elastic effects. Figures 4.7 - 4.12 exhibit the flow pattern of the PAA samples through the microfluidic device with the flow conditions defined in table 4.12.



(a) Point 1: 1000 PAA, channel 1:1, $Q=0.0270$ ml/h, $Re=7.24 \times 10^{-5}$ and $De=0.0266$

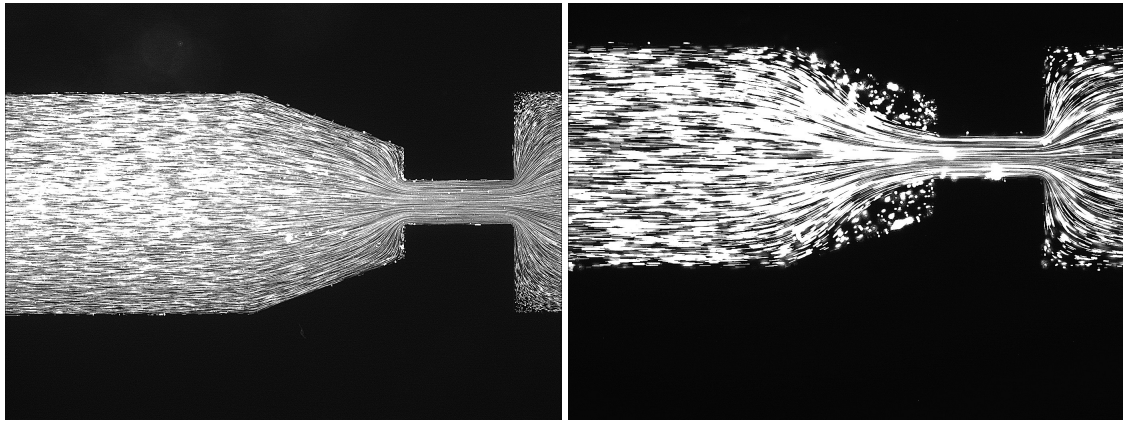
(b) Point 2: 1000 PAA, channel 1:2, $Q=0.0230$ ml/h, $Re=2.67 \times 10^{-4}$ and $De=0.0983$



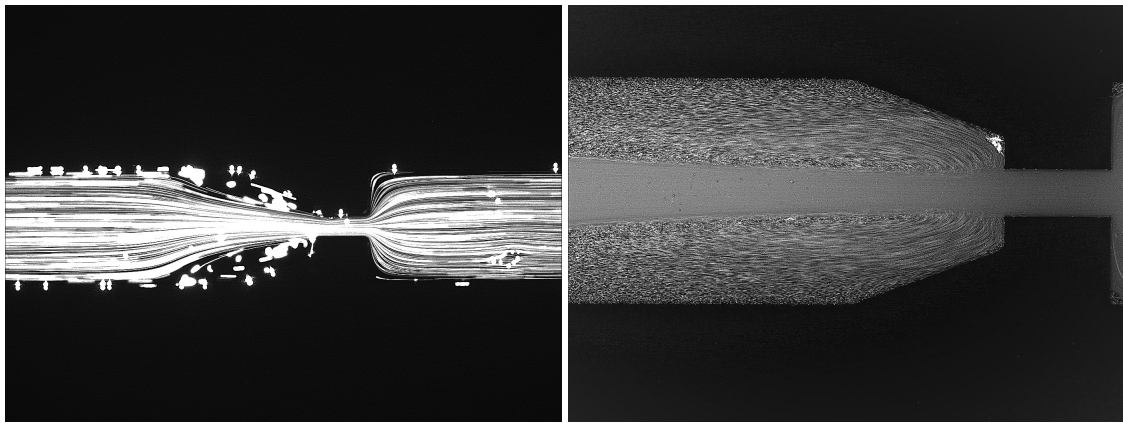
(c) Point 3: 1000 PAA, channel 1:1, $Q=0.0290$ ml/h, $Re=0.00513$ and $De=2.06$

(d) Point 4: 10000 PAA, channel 1:1, $Q=20.0$ ml/h, $Re=0.494$ and $De=223$

Figure 4.7: Flow pattern for $El=375$ at different conditions. The flow direction is from left to right

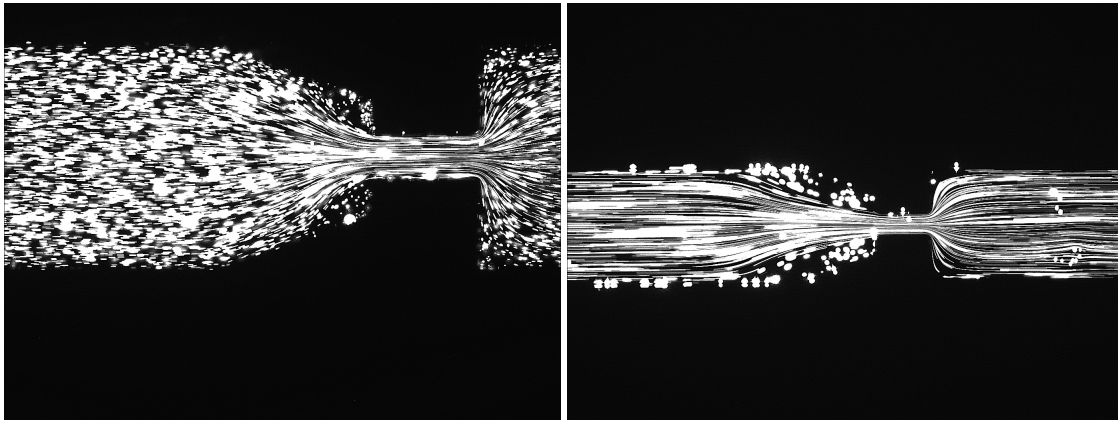


(a) Point 5: 1000 PAA, channel 1:1, $Q=0.0118$ ml/h, $Re=1.52 \times 10^{-5}$ and $De=0.0108$, (b) Point 6: 1000 PAA, channel 1:2, $Q=0.088$ ml/h, $Re=2.10 \times 10^{-4}$ and $De=0.166$

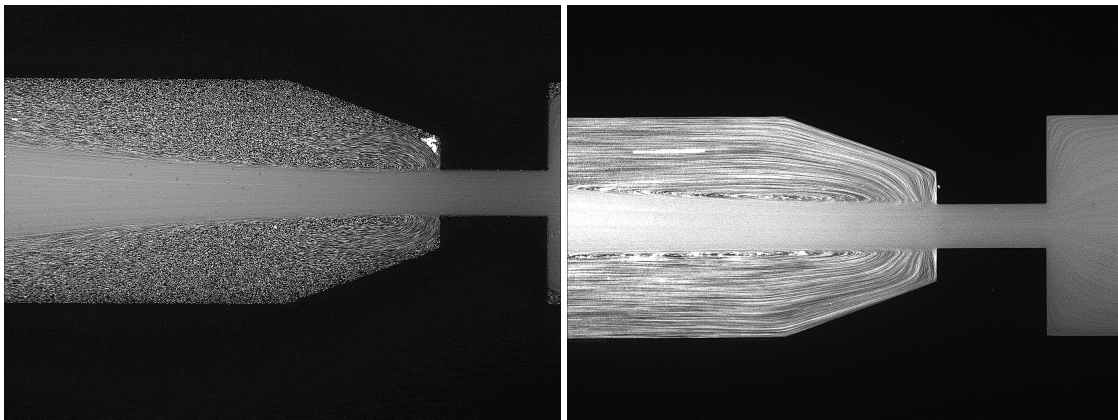


(c) Point 7: 1000 PAA, channel 1:8, $Q=0.096$ ml/h, $Re=8.30 \times 10^{-4}$ and $De=0.683$, (d) Point 8: 10000 PAA, channel 1:1, $Q=10.5$ ml/h, $Re=0.156$ and $De=117$

Figure 4.8: Flow pattern for $El=750$ at different conditions. The flow direction is from left to right

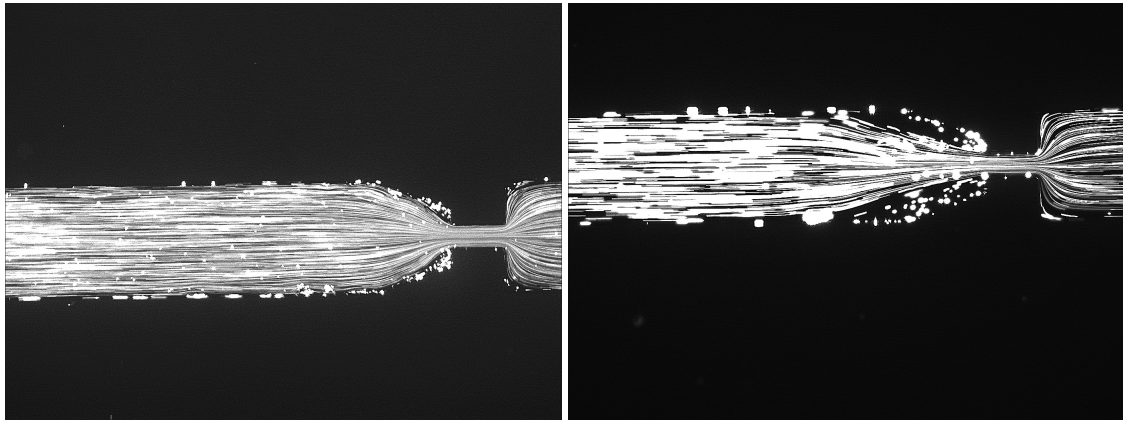


(a) Point 9: 1000 PAA, channel 1:4, $Q=0.0034$ ml/h, $Re=4.26 \times 10^{-5}$ and $De=0.0659$ (b) Point 10: 1000 PAA, channel 1:8, $Q=0.0035$ ml/h, $Re=1.50 \times 10^{-4}$ and $De=0.249$

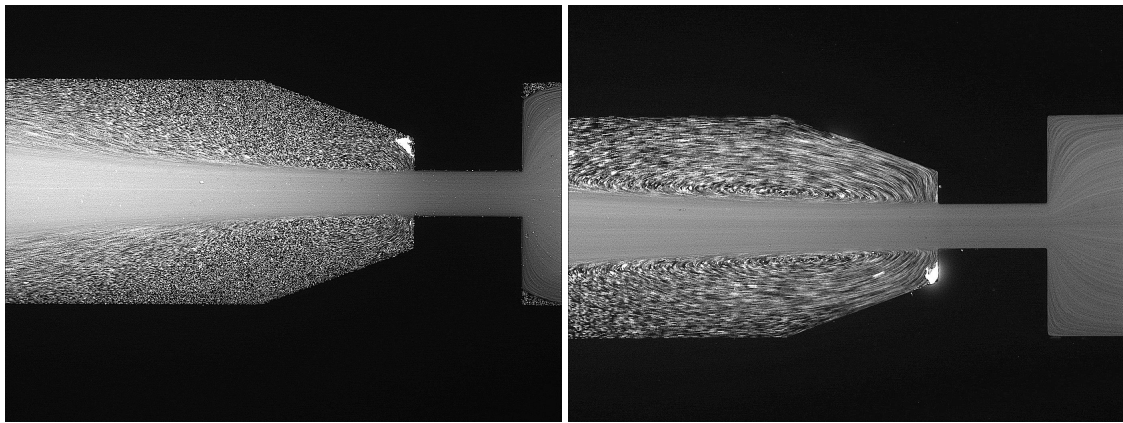


(c) Point 11: 10000 PAA, channel 1:1, $Q=4.52$ ml/h, $Re=0.0339$ and $De=50.5$ (d) Point 12: 10000 PAA, channel 1:2, $Q=3.44$ ml/h, $Re=0.111$ and $De=167$

Figure 4.9: Flow pattern for $El=1500$ at different conditions. The flow direction is from left to right

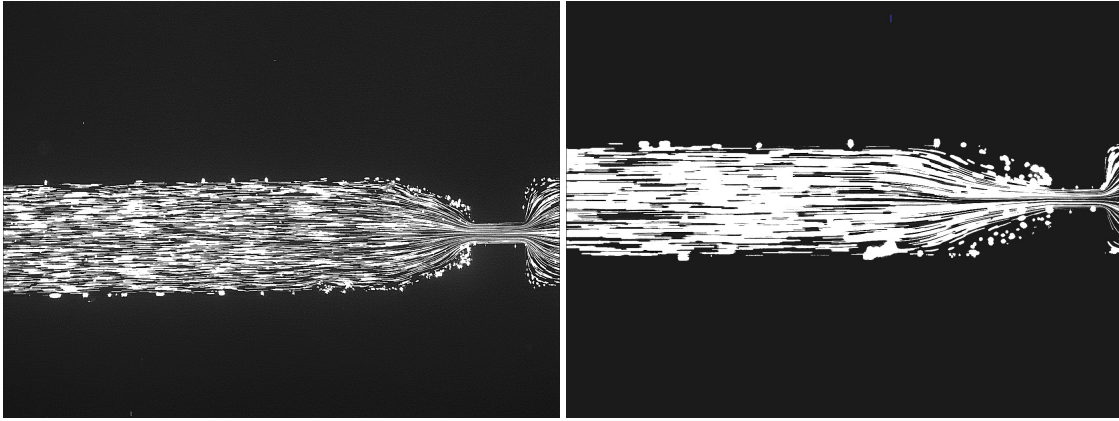


(a) Point 13: 1000 PAA, channel 1:4, $Q=0.0022$ ml/h, $Re=1.09 \times 10^{-5}$ and $De=0.0414$ (b) Point 14: 1000 PAA, channel 1:8, $Q=0.00235$ ml/h, $Re=7.54 \times 10^{-5}$ and $De=0.167$

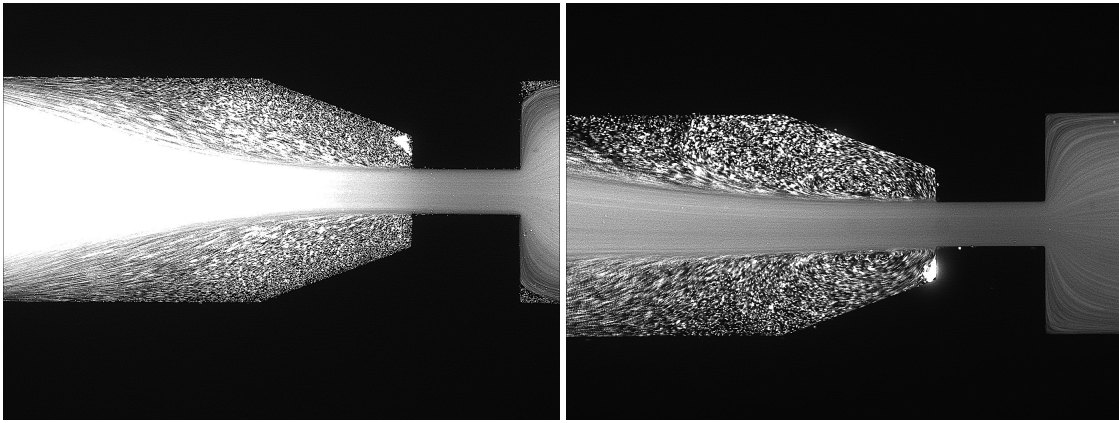


(c) Point 15: 10000 PAA, channel 1:1, $Q=3.14$ ml/h, $Re=0.0174$ and $De=35.1$ (d) Point 16: 10000 PAA, channel 1:2, $Q=2.36$ ml/h, $Re=0.0566$ and $De=115$

Figure 4.10: Flow pattern for $El=2020$ at different conditions. The flow direction is from left to right

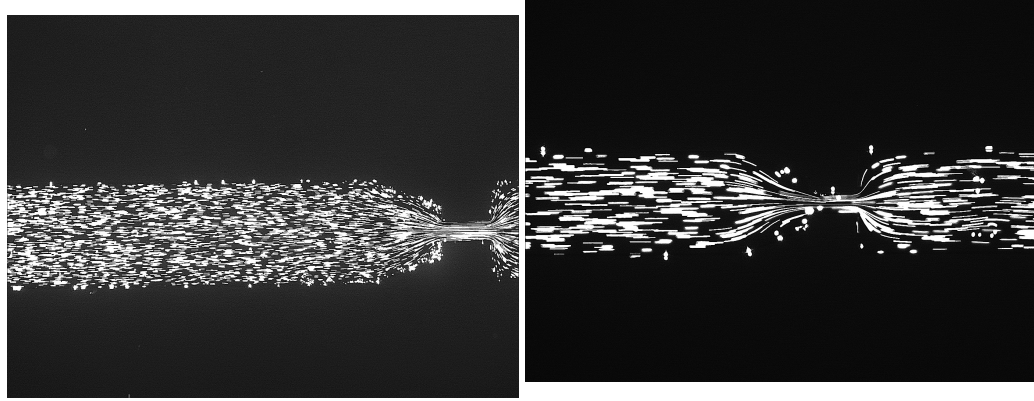


(a) Point 17: 1000ppm PAA+water, channel 1:4, (b) Point 18: 1000ppm PAA+water, channel 1:8,
 $Q=0.001$ ml/h, $Re=4.83 \times 10^{-6}$ and $De=0.0188$ $Q=0.001$ ml/h, $Re=1.72 \times 10^{-5}$ and $De=0.0712$



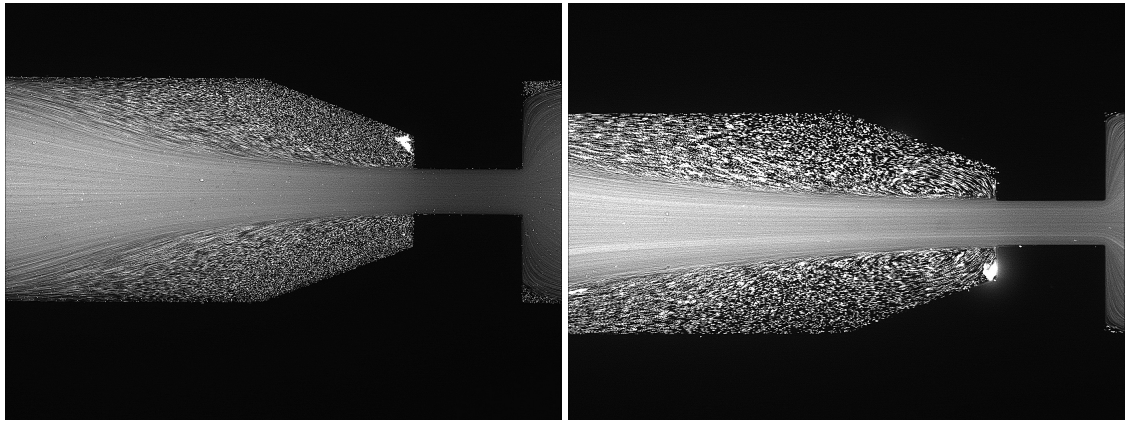
(c) Point 19: 10000ppm PAA+water, channel 1:1, (d) Point 20: 10000ppm PAA+water, channel 1:2,
 $Q=1.62$ ml/h, $Re=0.00518$ and $De=18.1$ $Q=2.36$ ml/h, $Re=0.0166$ and $De=58.2$

Figure 4.11: Flow pattern for $El=3500$ at different conditions. The flow direction is from left to right



(a) Point 21: 1000ppm PAA+water, channel 1:4, $Q=7.00\text{ml/h}$, $Re=2.59 \times 10^{-6}$ and $De=0.00131$

(b) Point 22: 1000ppm PAA+water, channel 1:8, $Q=1.00 \times 10^{-3}\text{ml/h}$, $Re=9.27 \times 10^{-5}$ and $De=0.0498$



(c) Point 23: 10000ppm PAA+water, channel 1:1, $Q=1.06\text{ ml/h}$, $Re=0.00237$ and $De=11.8$

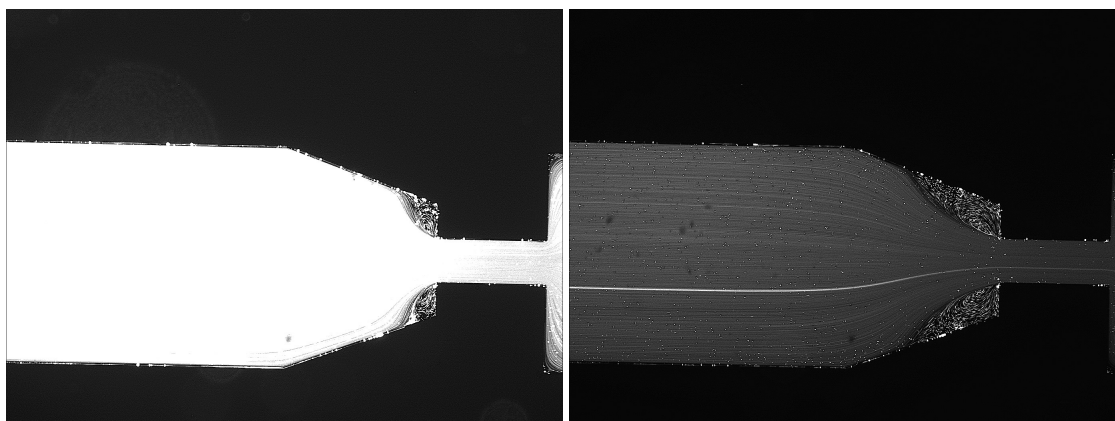
(d) Point 24: 10000ppm PAA+water, channel 1:2, $Q=0.780\text{ ml/h}$, $Re=0.00755$ and $De=37.9$

Figure 4.12: Flow pattern for $El=5000$ at different conditions. The flow direction is from left to right

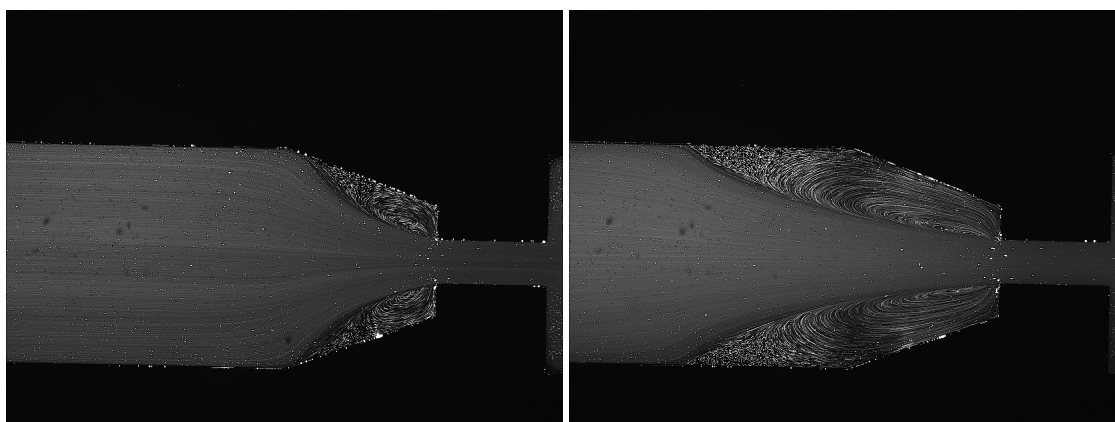
From the previous figures is possible to divide them into 3 different follow patterns. At lower Re and De , presented in points 1, 5, 17 and 21, the fluid maintains attached to the walls without a visible instability of vortex formation, revealing a Newtonian like behaviour for small Re . When Re and De are increased we enter in a second regime, where the fluid detaches from the walls of the micro-channel. At first view is not clear if in the corners we are in the presence of a dead zone without any flow as appears to be the case for example of figure 4.10b, or if we have a vortex formation with the fluid rotating very slowly as figure 4.8c appears to show. A dead zone is highly unlikely since it was only documented in the works of Kuzhir et.al. [75] and Alexandrou et.al. [76] however their work are with magnetorheological fluids and with fluids that exhibit Herschel-Bulkley viscoplastic behaviour respectively. When a non-Newtonian fluid is used a vortex creation becomes the most plausible outcome as shown in the works of Rothstein et.al [77]; Galindo-Rosales et.al. [78] and Sousa et.al. [79] where the formation of upstream vortices are evident and

with the increase in Re and De , strong vortex enhancement is observed.

So to prove that the observed flow patterns are created by upstream vortices, it was performed an experiment with 1000ppm PAA+water inside the 1:1 channel with an increasing flow rate. Again this experiment is only to prove the existence of a vortex upstream of the contraction and not to replicate any printing condition or El.



(a) 1000ppm PAA+water, channel 1:1, $Q=0.1$ ml/hr, $Re=7.00 \times 10^{-4}$ and $De=0.0982$ (b) 1000ppm PAA+water, channel 1:1, $Q=0.5$ ml/hr, $Re=0.0109$ and $De=0.491$



(c) 1000ppm PAA+water, channel 1:1, $Q=1$ ml/hr, $Re=0.0344$ and $De=0.982$ (d) 1000ppm PAA+water, channel 1:1, $Q=5$ ml/hr, $Re=0.423$ and $De=4.91$

Figure 4.13: Vortex generation and growing inside a micro-channel

The results in figure 4.13 show an vortex generation, at a very slow speed when compared with the centreline. To be able to visualise this phenomena it is necessary to increase the exposure time of the digital camera to about 5-10 seconds which is used to create a motion behaviour and track particles trajectory. To produce this effect is also necessary a correct concentration of particles. A high number of particle with a high exposure time would lead to an bright light without any outcome. Figure 4.13a almost illustrates one of this cases. As we decrease the scale, a smaller amount of particles can be fitted inside the channel which prevents us from getting the

recirculation areas, mainly at slower flow rates, giving a sensation of a non-flowing area near the corner as discussed previously.

For higher Re and De we can see a preferential central path and larger vortices due to the progressive enhancement of elastic effects, not only showing a bigger length but also its centre dislocating further left, away from the contraction as shown by figure 4.9d.

In terms of actual printing conditions, we can analyse for example point 14 and point 22 (figure 4.10b and 4.12b), since these points closer to a printing conditions, namely polycarbonate with a flow rate of $30 \text{ mm}^3/\text{s}$ and $10 \text{ mm}^3/\text{s}$, respectively. It is possible to observe a funnelled flow path, but as shown by 4.13, this is caused by an upstream vortices. Yet the printing conditions have a slightly higher De and Re which will potentiate even further the elastic effects resulting in even bigger vortices to the ones observed in those figures. These vortices cause three effects: the first is funnelled path as discussed before which leads a higher velocity at the centre line, resulting in an increased flow rate to the one programmed. Since the vortices rotate at very slow speed near the nozzle walls, it enhance a greater heat transfer through the nozzle walls, this means that a volume of material will have a lower temperature, resulting in a higher viscosity or an extreme case result in a solidification which could lead not only to an accumulation of material near the nozzle contraction creating a different and variable geometrical configuration of the real nozzle but also in extreme cases a clogging. Finally, since this material near the walls is rotating without being extruded, it accumulates creating a backflow effect with a possible material escape between the filament and the liquefier walls. Bigger the vortices leads to more material located near the walls that is not extruded, creating an even more significant effect.

Table 4.13: Experimental points and their corresponding dimensionless numbers exhibiting a laminar profile

	Re	De	El
Point 1	7.240×10^{-5}	2.657×10^{-2}	366.9
Point 5	1.515×10^{-5}	1.082×10^{-2}	714.2
Point 17	4.826×10^{-6}	1.882×10^{-2}	3900
Point 21	2.592×10^{-6}	1.317×10^{-2}	5084

In order to get the working points of Table 4.13 during the printing conditions without changing the design of the nozzle, it is necessary to change the working polymer. Using equations 3.42 and 3.51 it is possible to determine the viscosity, relaxation time of a polycarbonate and flow rate necessary to replicate these values in the real geometry. Table 4.14 presents, in a conceptual way, 3 possible polymer for each point presented in table 4.13, by varying the viscosity, relaxation time and flow rate needed to achieve the Re and De desired.

Table 4.14: Different polymer that can create a laminar profile inside a FDM 3D printing nozzle with the current geometrical configuration

	η [Pa.s]	λ [ms]	Q [mm ³ /s]	Re	De	El
Polymer 1	61.0	3.30	1.39	7.76×10^{-5}	0.0295	380
Polymer 2	488	0.410	11.1	7.77×10^{-5}	0.0293	378
Polymer 3	1.31×10^3	0.152	30.00	7.78×10^{-5}	0.0293	378
Polymer 4	300	1.32	1.39	1.58×10^{-5}	0.0118	748
Polymer 5	2.40×10^3	0.165	11.1	1.58×10^{-5}	0.0118	748
Polymer 6	6.48×10^3	0.0613	30.0	1.58×10^{-5}	0.0118	746
Polymer 7	763	2.43	1.39	6.20×10^{-6}	0.0217	3.50×10^3
Polymer 8	6.10×10^3	0.304	11.1	6.21×10^{-6}	0.0217	3.50×10^3
Polymer 9	1.65×10^4	0.112	30.0	6.20×10^{-6}	0.0216	3.49×10^3
Polymer 10	1.55×10^3	1.71	1.39	3.05×10^{-6}	0.0153	5.01×10^3
Polymer 11	1.24×10^3	0.214	11.1	3.05×10^{-6}	0.0153	5.01×10^3
Polymer 12	3.35×10^4	0.079	30.0	3.05×10^{-6}	0.0152	5.00×10^3

If we use the book "Handbook of Polycarbonate of Science and Technology" [51] as a source of available polycarbonate not all of the proposed solutions translate into a real one. And the ones that could represent a valid polycarbonate, namely Polymer 1, 2, 4, 7 and 10 exhibit a relative slow flow rate, which translates into a small printing speed, resulting in longer waiting time to achieve a final piece. So it may be necessary to change the geometrical configuration of the nozzle in order to decrease the vortex generation, leading to a higher Re and De while maintaining a laminar profile.

Chapter 5

Remarks and Further Work

In chapter 4, the results of the flow visualizations inside 4 micro-channels with different scales were analysed. The fabrication of these micro-channels was a complex process and required a considerable amount of time to produce a error free mask. The different scales gave an important flexibility in terms of replicating the printing conditions for different El numbers and so it was possible to create a map of flow patterns for this geometrical configuration. It was possible to record three different flow pattern zones, as shown in figure 5.1. At lower Re and De is possible to observe a laminar profile, very similar to a Newtonian fluid-flow where the fluid stays attached to the walls of the micro-channel without any disturbance. As the elastic effects are increased a second zone is visible where the flow detaches from the walls upstream of the contraction. This is due to the generation of corner vortices upstream the contraction. The typical printing conditions are located in this area where the vortices alters the flow conditions at the nozzle, resulting in a higher speed through the contraction than the one established. With an increase in the Re and De, so the vortices grow up to the point where we reach the third and final zone where large vortices promote a preferential central flow path. Additionally, these vortices upstream the contraction may be responsible for the backflow problem in the 3D printer.

As expected due to the elastic effects of the analogue fluids it was possible to observe the formation of vortices upstream of the contraction, leading to a volume of fluid rotating at lower velocity than the extruded one. This enhances heat transfer through the nozzle walls and near the contraction which could lead to a formation of solid pieces promoting clogging issues. Furthermore the vortex create a zone of under-extruded material, which can accumulate near the walls up to the point it escapes between the filament and liquefier resulting in a backflow effect which leads to a catastrophic failure in a FDM 3D printing process.

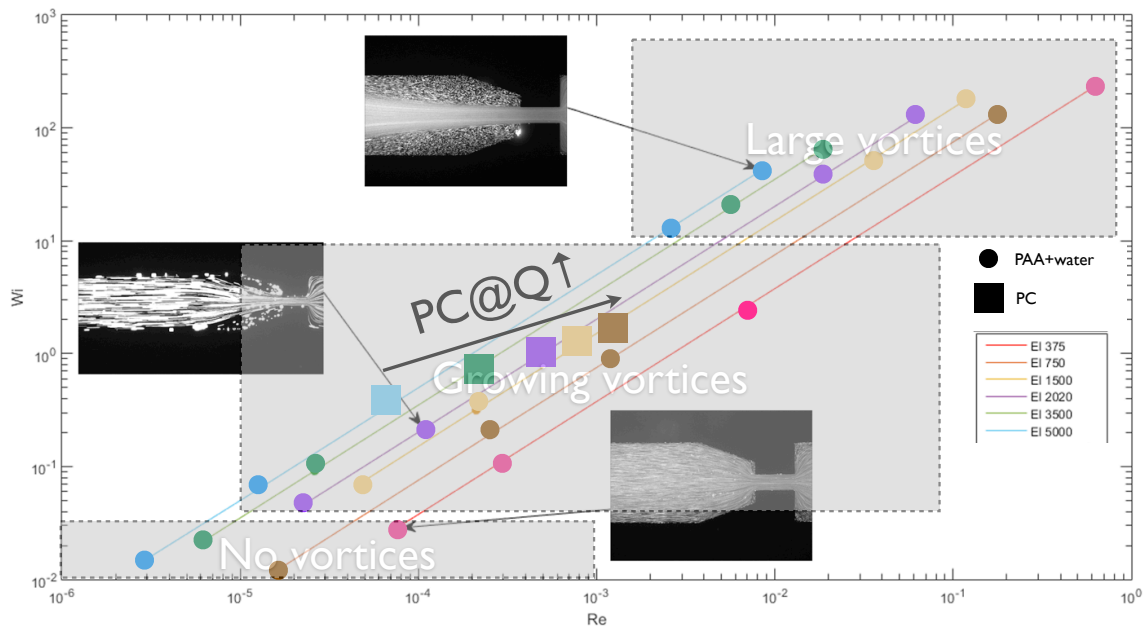


Figure 5.1: Flow pattern map resulting in different flow regimes

Since this work is a first approach to these type of problems, in future works it would be convenient to perform a proper rheological characterization of the polymer used in the FDM 3D printing, mainly a viscosity curve to accurately describe its shear-thinning behaviour and an extensional rheometry to determine its relaxation time. If a microfluidic approach is maintained, a wider range of analogue fluids should be produced, not only to complete even more the flow pattern map, but also to replicate the exact printing conditions and to discover the critical Re and De values that potentiates a laminar flow. Another approach could be creating different geometry configurations and analyse if any one of them retards or even prevents the vortex generation. Finally, and using all of this information, try replicate numerically the extruding process inside the 3D printing in terms of flow pattern and heat transfer.

References

- [1] ASTM Committee F42 on Additive Manufacturing Technologies and ASTM Committee F42 on Additive Manufacturing Technologies. Subcommittee F42. 91 on Terminology. *Standard terminology for additive manufacturing technologies*. ASTM International, 2012.
- [2] Y. Wang, R. Blache, and X. Xu. Selection of additive manufacturing processes. *Rapid Prototyping Journal*, 23(2):434–447, 2017.
- [3] B.N. Turner, R. Strong, and S. A. Gold. A review of melt extrusion additive manufacturing processes: I. process design and modeling. *Rapid Prototyping Journal*, 20(3):192–204, 2014.
- [4] H. K. Sezer and O. Eren. Fdm 3d printing of mwcnt re-inforced abs nano-composite parts with enhanced mechanical and electrical properties. *Journal of Manufacturing Processes*, 37:339 – 347, 2019.
- [5] M. Cotteleer and J. Joyce. 3d opportunity: Additive manufacturing paths to performance, innovation, and growth. *Deloitte Review*, 01 2014.
- [6] X. Wang, M. Jiang, Z. Zhou, J. Gou, and D. Hui. 3d printing of polymer matrix composites: A review and prospective. *Composites Part B: Engineering*, 110:442 – 458, 2017.
- [7] J. Cantrell, S. Rohde, D. Damiani, R. Gurnani, L. DiSandro, J. Anton, A. Young, A. Jerez, D. Steinbach, C. Kroese, et al. Experimental characterization of the mechanical properties of 3d-printed abs and polycarbonate parts. *Rapid Prototyping Journal*, 23(4):811–824, 2017.
- [8] H.K. Sezer and O. Eren. Fdm 3d printing of mwcnt re-inforced abs nano-composite parts with enhanced mechanical and electrical properties. *Journal of Manufacturing Processes*, 37:339 – 347, 2019.
- [9] E. L. Gilmer, D. Miller, C. A. Chatham, C. Zawaski, J. J. Fallon, A. Pekkanen, T. E. Long, C. Williams, and M. Bortner. Model analysis of feedstock behavior in fused filament fabrication: Enabling rapid materials screening. *Polymer*, 152, 11 2017.
- [10] M.S.N. Oliveira, M.A. Alves, and F. Pinho. *Microfluidic Flows of Viscoelastic Fluids Chapter 6 Pages 131-174*. John Wiley Sons Ltd, 2011.
- [11] R.E. Evans and K. Walters. Flow characteristics associated with abrupt changes in geometry in the case of highly elastic liquids. *Journal of Non-Newtonian Fluid Mechanics*, 20:11 – 29, 1986.
- [12] D. F. James. Boger fluids. *Annual Review of Fluid Mechanics*, 41(1):129–142, 2009.
- [13] M. A. Alves, F. T. Pinho, and P. J. Oliveira. Visualizations of boger fluid flows in a 4:1 square–square contraction. *AIChE Journal*, 51(11):2908–2922, 2005.

- [14] L. Campo-Deaño, F. J. Galindo-Rosales, F. T. Pinho, M. A. Alves, and M. S.N. Oliveira. Flow of low viscosity boger fluids through a microfluidic hyperbolic contraction. *Journal of Non-Newtonian Fluid Mechanics*, 166(21):1286 – 1296, 2011.
- [15] I. Gibson, D. Rosen, and B. Stucker. *Additive manufacturing technologies: 3D printing, rapid prototyping, and direct digital manufacturing, second edition*. 01 2015.
- [16] Jian-Yuan Lee, J. An, and C.Kai Chua. Fundamentals and applications of 3d printing for novel materials. *Applied Materials Today*, 7:120 – 133, 2017.
- [17] P. Eswaran, K. Sivakumar, and M. Subramaniyan. Minimizing error on circularity of fdm manufactured part. *Materials Today: Proceedings*, 5(2, Part 2):6675 – 6683, 2018. In: International Conference on Emerging Trends in Materials and Manufacturing Engineering (IMME17), March 10-12, 2017.
- [18] Ultimaker B.V. Developments and trends in 3d printing. <https://ultimaker.com/download/74242Developmentsandtrends3Dprinting.pdf>, 2018.
- [19] Ultimaker B.V. What is 3d printing. <https://ultimaker.com/en/explore/what-is-3d-printing>, February 2019.
- [20] O.S. Carneiro, A.F. Silva, and R. Gomes. Fused deposition modeling with polypropylene. *Materials & Design*, 83:768 – 776, 2015.
- [21] K. Bates-Green and T. Howie. Materials for 3d printing by fused deposition. http://www.materialseducation.org/educators/matedu-modules/docs/Materials_in_FDM.pdf, 2017.
- [22] Ultimaker V.B. Build plate adhesion: How to get your print to stick to the build plate. <https://ultimaker.com/en/resources/257-build-plate-adhesion-how-to-get-your-print-to-stick-to-the-build-plate>, March 2019.
- [23] F.A. Morrison. *Understanding Rheology*. Raymond F. Boyer Library Collection. Oxford University Press, 2001.
- [24] F.J. Galindo-Rosales. *Complex Fluid-Flows in Microfluidics*. Springer International Publishing, 06 2017.
- [25] J. M. Krishnan, A. P. Deshpande, and P.B.S. Kumar. *Rheology of complex fluids*. Springer, 2010.
- [26] P. Barman, RR Kairi, A. Das, and Md R. Islam. An overview of non-newtonian fluid. *International Journal of Applied Science and Engineering*, 4(2):97, 2016.
- [27] J. Mewis and N. J. Wagner. *Colloidal suspension rheology*. Cambridge University Press, 2012.
- [28] RheoSense. Viscosity of newtonian and non-newtonian fluids. <http://www.rheosense.com/applications/viscosity/newtonian-non-newtonian>, 2019.
- [29] T.G. Mezger. *Applied Rheology: With Joe Flow on Rheology Road*. Anton Paar GmbH, 2014.

- [30] R.B. Bird, R. C. Armstrong, and O. Hassager. Dynamics of polymeric liquids. vol. 1: Fluid mechanics. 1987.
- [31] G. Toth, D. Nagy, A. Bata, and K. Belina. Determination of polymer melts flow-activation energy a function of wide range shear rate. *Journal of Physics: Conference Series*, 1045:012040, 06 2018.
- [32] R. Poole. Deborah and weissenberg numbers. *The British Society of Rheology - Rheology Bulletin*, 53:32–39, 06 2012.
- [33] The inertio-elastic planar entry flow of low-viscosity elastic fluids in micro-fabricated geometries. *Journal of Non-Newtonian Fluid Mechanics*, 129(1):1 – 22, 2005.
- [34] HK Nason. A high temperature, high pressure rheometer for plastics. *Journal of Applied Physics*, 16(6):338–343, 1945.
- [35] RS Spencer and RE Dillon. The viscous flow of molten polystyrene. *Journal of colloid science*, 3(2):163–180, 1948.
- [36] J. Musil and M. Zatloukal. *Entry flow vortices in polymer melt extrusion: A review*, volume 1843. 2017.
- [37] T. F Ballenger, I-J. Chen, J. W. Crowder, G. Hagler, D. Bogue, and J. White. Polymer melt flow instabilities in extrusion: investigation of the mechanism and material and geometric variables. *Transactions of the Society of Rheology*, 15(2):195–215, 1971.
- [38] SA White and DG Baird. The importance of extensional flow properties on planar entry flow patterns of polymer melts. *Journal of Non-Newtonian Fluid Mechanics*, 20:93–101, 1986.
- [39] H. Münstedt, M. Schwetz, M. Heindl, and M. Schmidt. Influence of molecular structure on secondary flow of polyolefin melts as investigated by laser-doppler velocimetry. *Rheologica acta*, 40(4):384–394, 2001.
- [40] M. Schwetz, Helmut Münstedt, M. Heindl, and A. Merten. Investigations on the temperature dependence of the die entrance flow of various long-chain branched polyethylenes using laser-doppler velocimetry. *Journal of Rheology*, 46:797–815, 07 2002.
- [41] G. H. McKinley, L. Rodd, M. SN Oliverira, and J. Cooper-White. Extensional flows of polymer solutions in microfluidic converging/diverging geometries. *Journal of Central South University of Technology*, 14(1):6–9, 2007.
- [42] G. J. Sommer, D. S. Chang, A. Jain, S. M. Langelier, J. Park, M. Rhee, F. Wang, R. I. Zeitoun, and M. A. Burns. Introduction to microfluidics.
- [43] C. J. Pipe and G. H. McKinley. Microfluidic rheometry.
- [44] X. Hu, P. E. Boukany, O. L Hemminger, and L. J. Lee. The use of microfluidics in rheology. *Macromolecular Materials and Engineering*, 296(3-4):308–320, 2011.
- [45] Y. Dinic, J. and Zhang, L. Nallely Jimenez, and V. Sharma. Extensional relaxation times of dilute, aqueous polymer solutions. *ACS Macro Letters*, 4(7):804–808, 2015.
- [46] K. Liu and Z. H. Fan. Thermoplastic microfluidic devices and their applications in protein and dna analysis. *Analyst*, 136(7):1288–1297, 2011.

- [47] P. Kim, K. W. Kwon, M. C. Park, S. H. Lee, S. M. Kim, and K. Y. Suh. Soft lithography for microfluidics: a review. 2008.
- [48] S. D. Minteer. *Microfluidic techniques: reviews and protocols*, volume 321. Springer Science & Business Media, 2006.
- [49] G.F. Baumann and S. Steingiser. Rheological measurements on polycarbonate. *Journal of Polymer Science Part A: General Papers*, 1(11):3395–3406, 1963.
- [50] Polymaker. Technical data sheet, pc max. https://polymaker.com/Downloads/TDS/PolyMax_PC_TDS_V4.pdf.
- [51] J.T. Bendler. *Handbook of polycarbonate science and technology*. CRC press, 1999.
- [52] AV Shenoy, DR Saini, and VM Nadkarni. Melt rheology of polymer blends from melt flow index. *International Journal of Polymeric Materials*, 10(3):213–235, 1984.
- [53] M. Delgado, S. Secouard, C. Valencia, and J. Franco. On the steady-state flow and yielding behaviour of lubricating greases. *Fluids*, 4:6, 01 2019.
- [54] *Comprehensive Polymer Science and Supplements*. Elsevier Science, 1996.
- [55] K. Hyun, M. Wilhelm, C. Klein, K. S. Cho, J. Gun Nam, K. Ahn, S. Lee, R. Ewoldt, and G. Mckinley. A review of nonlinear oscillatory shear tests: Analysis and application of large amplitude oscillatory shear (laos). *Progress in Polymer Science - PROG POLYM SCI*, 36:1697–1753, 12 2011.
- [56] F. Del Giudice, S.J. Haward, and A. Q. Shen. Relaxation time of dilute polymer solutions: A microfluidic approach. *Journal of Rheology*, 61(2):327–337, 2017.
- [57] J.A. Covas, J.F. Agassant, A.C. Diogo, J. Vlachopoulos, and K. Walters. *Rheological fundamentals of polymer processing*, volume 302. Springer Science & Business Media, 2013.
- [58] F. Galindo-Rosales, J.P. Segovia Gutiérrez, F. Pinho, Manuel Alves, and J. de Vicente. Extensional rheometry of magnetic dispersions. *Journal of Rheology*, 59:193–209, 01 2015.
- [59] L. Campo-Deaño. Shear and extensioal rheometry.
- [60] F. Stadler. What are typical sources of error in rotational rheometry of polymer melts. *Korea-Australia Rheology Journal*, 26:277–291, 08 2014.
- [61] R. H. Ewoldt, M. T. Johnston, and L. M. Caretta. Experimental challenges of shear rheology: how to avoid bad data. In *Complex fluids in biological systems*, pages 207–241. Springer, 2015.
- [62] N. Phan-Thien and N. Mai-Duy. *Understanding Viscoelasticity: An Introduction to Rheology*. 01 2017.
- [63] T.L. Bergman, F.P. Incropera, D.P. DeWitt, and A.S. Lavine. *Fundamentals of heat and mass transfer*. John Wiley & Sons, 2011.
- [64] P. Jacob Eravuchira. *Lithographic Micro-and Nanostructuring of SU-8 for Biotechnological Applications*. PhD thesis, Universitat Rovira I Virgil, 2015.

- [65] Elveflow. How to choose the right plasma cleaner for the pdms bonding of your microfluidic chip? <https://www.elveflow.com/microfluidic-tutorials/soft-lithography-reviews-and-tutorials/how-to-choose-your-soft-lithography-instruments/pdms-soft-lithography-plasma-cleaner/>.
- [66] D. Fuard, T. Tzvetkova-Chevolleau, S. Decossas, P. Tracqui, and P. Schiavone. Optimization of poly-di-methyl-siloxane (pdms) substrates for studying cellular adhesion and motility. *Microelectronic Engineering*, 85(5-6):1289–1293, 2008.
- [67] G. Giusteri and R. Seto. A theoretical framework for steady-state rheometry in generic flow conditions. *Journal of Rheology*, 62:713, 05 2018.
- [68] P.J. Oliveira and F.T. Pinho. Pressure drop coefficient of laminar newtonian flow in axisymmetric sudden expansions. *International Journal of Heat and Fluid Flow*, 18(5):518 – 529, 1997.
- [69] F. Delplace. Laminar flow of newtonian liquids in ducts of rectangular cross-section a model for both physics and mathematics. *Open Access Journal of Mathematical and Theoretical Physics*, 1:198–201, 09 2018.
- [70] H. Meeuw, V. Wisniewski, and B. Fiedler. Frequency or amplitude?—rheo-electrical characterization of carbon nanoparticle filled epoxy systems. *Polymers*, 10:999, 09 2018.
- [71] P. Zoller. A study of the pressure-volume-temperature relationships of four related amorphous polymers: Polycarbonate, polyarylate, phenoxy, and polysulfone. *Journal of Polymer Science: Polymer Physics Edition*, 20(8):1453–1464, 1982.
- [72] P.C. Sousa, E.J. Vega, J.M. Sousa, R., and M. A. Alves. Measurement of relaxation times in extensional flow of weakly viscoelastic polymer solutions. *Rheologica Acta*, 56(1):11–20, 2017.
- [73] B. Xiong, R. Dettam Loss, D. Shields, T. Pawlik, R. Hochreiter, A. Zydney, and M. Kumar. Polyacrylamide degradation and its implications in environmental systems. *npj Clean Water*, 1, 12 2018.
- [74] S. Saravanan, J.A. Reena, J.R. Rao, T. Murugesan, and B.U. Nair. Phase equilibrium compositions, densities, and viscosities of aqueous two-phase poly(ethylene glycol) + poly(acrylic acid) system at various temperatures. *Journal of Chemical & Engineering Data*, 51(4):1246–1249, 2006.
- [75] P. Kuzhir, M. López-López, and G. Bossis. Abrupt contraction flow of magnetorheological fluids. *Physics of Fluids*, 21, 05 2009.
- [76] A.N.Alexandrou, T.M.McGilvrey, and G. Burgos. Steady herschel–bulkley fluid flow in three-dimensional expansions. *Journal of Non-Newtonian Fluid Mechanics*, 100(1):77 – 96, 2001.
- [77] J.P. Rothstein and G.H. McKinley. The axisymmetric contraction–expansion: the role of extensional rheology on vortex growth dynamics and the enhanced pressure drop. *Journal of Non-Newtonian Fluid Mechanics*, 98(1):33 – 63, 2001.
- [78] F.J.Galindo-Rosales, L. Campo-Deaño, P. C. Sousa, Vera M. Ribeiro, M.S.N. Oliveira, M.A. Alves, and F.T. Pinho. Viscoelastic instabilities in micro-scale flows. *Experimental Thermal and Fluid Science*, 59:128 – 139, 2014.

- [79] P.C. Sousa, P.M. Coelho, M.S.N. Oliveira, and M.A. Alves. Effect of the contraction ratio upon viscoelastic fluid flow in three-dimensional square–square contractions. *Chemical Engineering Science*, 66(5):998 – 1009, 2011.