TAMPERE UNIVERSITY OF TECHNOLOGY

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ROTATIONAL MELT SPINNING AS A MANUFACTURING METHOD FOR TISSUE ENGINEERING SCAFFOLDS

Master of Science Thesis

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ABSTRACT

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Nanoscale fibers and non-woven mats have increasing demand in biomedical applications like in tissue engineering. They are reported to mimic natural tissue environment and act as cell growth promoting substrates due to fiber diameters are in same magnitude with fibrils of extracellular matrix. Nanofibers are commonly fabricated by electrospinning, where polymer is dissolved into solvent and spun into fibers using electric field. As disadvantage, solvents are often harmful or toxic.

A solvent-free rotational melt spinning method (RMS) was studied as a manufacturing method of sub-micron sized fibers or fibrous webs. RMS method consists of melting of polymer and pushing it through a spinning nozzle using centrifugal forces. Critical processing parameters were studied in this work. Trials were done by a commercial table sized device with constant rotation speed of 2800 rpm. The device was modified and three different spinnerets and two collectors were used. Thermoplastic biodegradable polymers poly(L-lactide-co-D-lactide) 96/4, poly-DL-lactide 50/50, poly-ε-caprolactone and poly(L-lactide/ε-caprolactone) 70/30 with different inherent viscosities (iv) and melting ranges had been processed.

Material properties like elasticity and crystallinity, the spinneret design and processing parameters like heating and cooling affected the size and structure of formed fibrous product. End-products varied from separate and short fibers to fibrous webs with average fiber diameters between 5-15 μm. Present results showed that RMS is a promising method to produce sub-micron sized webs for tissue engineering purposes but stretching of fibers into sub-micron size and repeatability of the process were challenging with the existing device. As future measures the spinning device should develop further by increasing the rotation speed of the spinneret and integrating a proper thermoelement into the device to improve controlling of parameters and repeatability of process.

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Nanokuitujen ja kuitukankaiden käyttö kasvaa biolääketieteen sovelluskohteissa, kuten kudosteknologiassa. Kuidut ovat halkaisijaltaan samaa kokoluokkaa kuin fibrillit solunulkoisessa väliaineessa ja niiden on todettu jäljittelevän luonnollista kudosympäristöä ja edistävän solujen kasvua rakenteessa. Yleisesti nanokuituja valmistetaan sähkökehruulla, jossa polymeeri liuotetaan liuottimeen ja kehrätään kuiduksi sähkökentän avulla. Huonona puolena menetelmässä on haitallisten ja jopa myrkyllisten liuotinaineiden käyttö.

Tässä työssä tutkittiin mikro- ja nanokuitujen valmistamista rotaatiosulakehruulla, jossa polymeeri on liuottamisen sijasta sulatettu ja kehrätty kuiduksi. Menetelmässä rotaatiovoimat työntävät sulan materiaalin muodon antavan kehruusuuttimen läpi. Tutkimus tehtiin kaupallisella pöytäkokoisella laitteistolla, jonka kehruusuuttimen pyörimisnopeus oli 2800 rpm. Tärkeät prosessiparametrit määritettiin ja laitteistoa muutettiin polymeerien prosessointiin paremmin soveltuvaksi. Tutkimuksessa käytettiin neljää termoplastista polymeeriä, poly(L-laktidi-co-D-laktidi) 96/4:sta, poly-DL-laktidi 50/50:sta, poly-ε-kaprolaktonia ja poly(L-laktidi/ε-kaprolaktoni) 70/30:sta.

Materiaaliominaisuuksien, kuten elastisuuden ja kiteisyyden, kehruusuuttimen muotoilun ja prosessiparametrien, kuten lämmityksen ja jäähdytyksen todettiin vaikuttavan lopputuotteen muotoon ja kuitupaksuuksiin. Irrallisia kuituja ja toisiinsa liimautuneista kuiduista muodostuneita kuitukankaita onnistuttiin valmistamaan. Yleisesti kuitupaksuudet vaihtelivat 5–15 μm välillä. Tulokset osoittavat, että rotaatiosulakehruu on potentiaalinen menetelmä mikro- ja nanokuitujen ja kuituverkkojen valmistamiseen, mutta prosessoinnin toistettavuus ja kuitujen venyttäminen nanokuiduiksi ei onnistunut nykyisellä laitteistolla. Jatkotoimenpiteenä laitteistoa tulisi kehittää lisäämällä kierrosnopeutta ja yhdistämällä laitteistoon lämpötilan säätämiseen ja mittaamiseen soveltuvan termoelementin, jotta prosessoinnin ohjattavuus ja toistettavuus paranisivat.

PREFACE

This master's thesis is made at Tampere University of Technology in department of Biomedical Engineering. The work is related to the research study of BioMediTech, a joint life science institute of Tampere University and Tampere University of Technology, and it is partly funded by Textile project of the biomaterials research group.

I would like to express my gratitude to my supervisor Anne-Marie Haaparanta for her guidance and support during my work. And I would like to thank my examiner professor Minna Kellomäki for offering me this great opportunity to take part in the interesting research study and giving valuable feedback. In addition, I would like to thank personnel of the department for helping me during my work. Especially I would like to express my gratitude to personnel of workshop for their know-how which made the work possible to carry out. Finally I would thank The Federation of Finnish Textile and Clothing Industries, Finatex, for supporting my studies by a grant.

Tampere, 26th May 2013

Kaisa Laine

CONTENTS

ABBREVIATIONS, TERMS AND NOTATION

CFS	confined feed system
CMS	centrifugal melt spinning
Forcespinning^{TM}	rotational spinning method developed at University of Texas
iv	inherent viscosity, the unit is dl/g
micron	linear measurement equal to one millionth of a meter
microfiber	a fiber with diameter of $10^{-4} - 10^{-7}$m
nanofiber	a fiber with diameter of 1–100 nm, $10^{-8} - 10^{-10}$m
non-woven	Textile structure which is formed straight from fibers without yarn preparation. Fibers can be tight together mechanically or chemically.
Obs	orifice band spinneret
PCL	poly-ε-caprolactone
PDLA 50/50	poly-DL-lactide
PLA	polylactide, polylactic acid based polymer
PLCL 70/30	poly(L-lactide/ε-caprolactone) 70/30
PLDLA 96/4	poly-96L/4D-lactide
PTFE	polytetrafluoroethylene, a synthetic fluoropolymer of tetrafluoroethylene
RJS	rotary jet-spinning
RMS	rotational melt spinning
rpm	unit of rotation speed, revolutions per minute
scaffold	supporting structure, cell bed
SEM	scanning electron microscopy
SmTf	steel mould spinneret with tapering furrows
SmWf	steel mould spinneret with widening furrows
sub-micron	something shorter or smaller than one millionth of a meter
T_g	glass transition temperature
T_m	melting point
TmTf	PTFE mould spinneret with tapering furrows
UFS	unconfined feed system

1. INTRODUCTION

Tissue engineering is a multidisciplinary field which is becoming more important cure beside of drugs and surgery. The aim of the tissue engineering is to create living and functional tissues and organs which can be used to replace or repair malfunctioning tissues. Tissue engineering and tissue repair combines biomaterials, cells and engineering methods which together with biochemical and physio-chemical factors are used to restore or improve biological functions. Biomaterials are used as scaffolds which are structural part of cellular composites. Biomaterials act as extracellular material which promote cell attachment, proliferation and differentiation but also construct structural support for cells. Chemical properties can be introduced by material selection when the scaffold architecture introduce physical and mechanical properties.

Scaffolds are three dimensional and porous structures which act as cell growth beds. High porosity and interconnected pore structure are desired. The porosity and a microstructure of the scaffold are important for cell ingrowth and transportation of nutrients and gases through the hole structure. Fiber materials is one option to produce porous structures. Nanoscale fibers and non-woven nanofibrous mats have increased demand in biomedical applications like in tissue engineering, biosensors, filtration, wound dressings and drug delivery. Nanofibrous materials are interesting alternatives for scaffolds due to high surface area to volume, low mass and small pore sizes and good mechanical properties. In tissue engineering nanofibrous scaffolds have reported to promote positively cell-matrix and cell-cell interactions and enabling normal phenotypic shape and gene expression in cells. Fiber diameter scale is in same magnitude with fibrils of extracellular matrix and for that reason the nanofibrous material well mimic natural tissue environment and act as cell growth promoting substrate.

Electrospinning is the most used method to produce nanofibers or nanofibrous non-woven webs but the technique has a few disadvantages. Electrospinning is slow and expensive method but the biggest disadvantage is a usage of harmful solvents. Solvent residues are forbidden in tissue engineered applications. For these reasons, solvent-free and high production rate rotational melt spinning technique is studied. One aim of this study is to figure out whether the rotational melt spinning could replace or be as an alternative to the electrospinning method.

Rotational melt spinning is quite novel fiber spinning method and only small number of publications exist. First publications are released in 2010 when Badrossamay et al. from Harvard University and Sarkar et al. from University of Texas Pan American have reported fiber fabrication methods based on rotation motion. Badrossamay et al. have studied fiber spinning using polymer solutions when Sarkar et al. have used polymer solutions and melts. Next year, in 2011, Huttunen and Kellomäki from Tampere University of Technology and Wang et al. as a collaboration of Kyoto University and Ecole Normale Supérieure have published articles about fiber fabrication by centrifugal spinning. Polymer melts are used in both studies. Best and most extensive results are achieved by Sarkar et al. who have reported that centrifugal spinning enables nanofiber fabrication from several polymers.

In this study, the aim is to study rotational melt spinning as manufacturing method for tissue engineered scaffolds. The first objective is to find out critical parameters and modify an existing device to be suitable for processing of polymers and the second objective is to determine processing parameters for each polymer. The main purpose is to fabricate nanofibrous material for further research studies. Theoretical background of this study is presented in Chapter 2. Materials, devices and device modifications, as well as processing variations are presented in Chapter 3. Spinning processes are first sorted by device configuration and secondly according to used polymers. Results are presented in Chapter 4 and they are followed by a discussion. Finally in Chapter 5 is a short summary of the hole study and also possible future measures are presented.

2. THEORY

2.1 Biodegradable polymers

Biodegradable polymers are polymers which undergo biodegradation occurring through biochemical reactions or the actions of micro-organisms. The main chain of polymer contain labile bonds which undergo bond scission resulting to naturally occurring lower molecular weight end-products. Biodegradable polymers can be divided into hydrolytically or enzymatically degradable polymers and most of them degrade via hydrolysis or via both degradation pathways. According to their origin, biodegradable polymers can be divided into synthetic or natural based polymers. Synthetic polymers includes e. g. poly-α-esters, like polyglycolides and polylactides and poly-ε-caprolactone when natural based polymers include polysacharides like chitin, chitosan, starch and cellulose. A few synthetic biodegradable thermoplastic polymers are discussed in more detail. [9; 33]

2.1.1 Polylactides

Polylactides, PLAs, are aliphatic, semi-crystalline or amorphous, polyesters which belong to the group of most used biopolymers in terms of volume [17]. The usability is result of good mechanical properties along with easy processability and controllable degradation properties. Polylactides are formed from chiral lactic acid monomers with two optically active configurations, D- and L-enantiomers. Polymerization of lactides leads to formation of three different isomers, L-, D- and DL-isomers, with different properties. In general, L-lactides forms crystalline polymers and presence of D-lactides increases the amorphous nature of polymers. Usually polylactides are semi-crystalline, but polymerization of racemic (D,L)-lactide mixture, which contain equal amount of left- and right-handed enantiomers, result to formation of optically in active mesolactides and an amorphous polymer. The chemical structure of PLA is presented in Figure 2.1. [6; 22; 33]

Properties of PLAs are able to tailor by varying a ratio of lactic isomers, a molecular weight and a degree of crystallinity. In general, polylactides are high strength thermally processable polymers with low elongation and high modulus. PLLA which is polymerized from L-lactides is a crystalline polymer with crystallinity degree of about 70 %. A glass transition temperature of PLLA, T_g, is around $60 - 65\,^{\circ}\mathrm{C}$ and

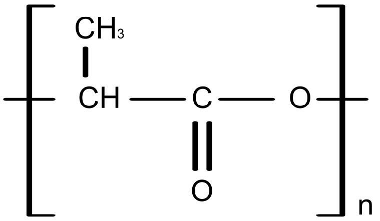


Figure 2.1: *Chemical structure of polylactide. [33]*

the melting point, T_m, is around $175 - 180\,^\circ C$. PLLA has good tensile strength of 15.5-150 MPa and low ultimate elongation of 3-10 %. The modulus of elongation is high, approximately 4.8 GPa. PLLA is hydrophobic but it undergoes hydrolytic bulk degradation. The strength retention is good due to very low degradation rate and that the strength of polymer decrease slower than the molar mass. The strength of PLLA is reduced after 6 months but complete degradation in the body can take from 2 to over 5 years. [6; 22; 33]

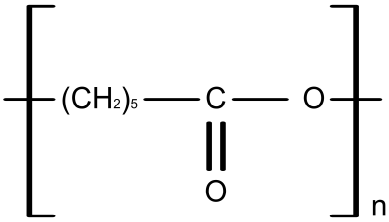
An introduction of even small amounts of D-lactide into the polymer chain decrease the polymer crystallinity. Poly(DL-lactide), PDLLA, is amorphous polymer which contain random distribution of L- and D-lactides. T_g is around $50 - 60\,^\circ C$ which little lower than T_g of PLLA and due to the amorphous nature of the PDLLA, a melting point do not exist. Mechanical properties of amorphous polymers are lower than properties of crystalline polymers. The tensile strength of PDLLA is 27.6-50 MPa and the modulus of elongation is 1.9 GPa which is much lower than the modulus of PLLA. PDLLA also undergoes bulk erosion and loose strength and mass faster than PLLA. The strength is reduced after 1-2 months and the complete degradation of the polymer takes 12-16 months. [6; 22; 33]

Basically the molecular weight of polymer along with the composition affect the ability of the polymer to crystallize and further to mechanical, physical and chemical properties. Crystallinity improves chemical stability of the polymer leading to decrease of water absorption and swelling of polymer. This results to the decrease of the rate of biological degradation. Hydrolytic degradation takes place first in amorphous phase of the polymer. A scission of polymer backbone occurs via breakage of ester linkages and results to non-toxic degradation products. [6; 17; 22; 33]

Thermal processing and solvent processing are both possible to lactide based polymers. Solubility is dependent on molecular weight and degree of crystallinity. [22] PLLA can be dissolved into chloroform and methylene chloride when PDLLA dissolves into the most of the organic solvents. In thermal processing, polymer crystallinity and molecular weight affect the melting temperature of the polymer and that way to suitable processing temperatures. The morphology and the molar mass of the end-product is determined during thermal processing. In case of fiber spinning, melt spun fibers have lower mechanical strength compared to solvent spun due to thermal degradation which occurs during melt spinning. [22] PLAs are permeable for water vapor and because water can cause enhanced polymer degradation during thermal processing, pre-drying of polymer is needed and processing time in machine should be as short as possible. Cooling rate also has influence in the morphology of end-products. Crystallization takes time and long cooling time may be required when formation of highly crystalline end-product is desired. [17]

2.1.2 Poly-ε-caprolactone

Polycaprolactone, PCL, belongs to the group of aliphatic polyesters like PLAs and it is composed of ε-caprolactone monomers. PCL is semi-crystalline polymer and crystallinity of PCL depends on the molecular weight and the ratio and distribution of ester and ethene building blocks in polymer backbone. The chemical structure is presented in Figure 2.2. [17; 33]



$$\left[(CH_2)_5 - \underset{\underset{O}{\|}}{C} - O \right]_n$$

Figure 2.2: *Chemical structure of poly-ε-caprolactone [33].*

PCL has low glass transition temperature and melting point due to low interactions between molecules and easy mobility of chain segments. T_g is $-60\,°C$ and T_m is around $59 - 64\,°C$. Thermal stability is high and PCL is suitable for melt processing. Also solvent processing is possible due to PCL can be dissolved into organic solvents. PCL is very elastic and it is more often used as a component of blends or copolymers than as pure polymer. PCL has modulus of elasticity of 0.2-0.4 GPa with tensile strength of 2.7-42 MPa and ultimate elongation of 300-1000 %. Density of PCL is relatively low compared to other biopolymers, it is 1.1 g/cm^3. Low molecular weight PCL, M_w less than 15 000 g/mol, can be brittle when high molecular weight PCL, M_w in range of 40 000 g/mol, is soft material. PCL is not suitable for high load bearing applications but it has been used in long term drug delivery and as long-lasting absorbable sutures. Pure PCL undergoes slow degradation which first occurs as hydrolytic degradation of aliphatic ester bonds and carry on as enzymatic degradation. Degradation takes 2-4 years. To achieve faster degradation of the polymer, PCL can be copolymerized with lactides. [17; 21; 58]

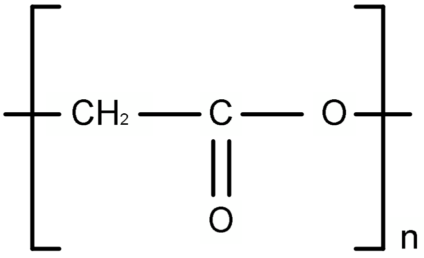
2.1.3 Poly(L-lactide/caprolactone)copolymers

Poly(L-lactide/caprolactone), PLCL, is a copolymer of l-lactide units and ε-caprolactone units. PLCL is a semi-crystalline polymer where hard L-lactide domains are able to form crystals and soft ε-caprolactone units enhance mobility of lactide units. PLCL has physically cross-linked structure which results in rubber-like elastic behaviour. Copolymerization of lactide and caprolactone results controlling of mechanical properties, shape-memory behaviour, degradation rate, drug-release properties. [20; 25; 58]

Properties of PLCL depends on the caprolactone and lactide contents in copolymer. Presence of caprolactone in PLCL improves elongation at break values and PLCL can have elongation of 200 % and a recovery in tension can be over 85 %. Crystallinity and crystallizability of PLCL decrease when caprolactone content or molecular weight increase. At the same time tensile modulus decreases, T_m and T_g decrease. Lactide and caprolactone units have different degradation times and for that reason it is possible to control degradation rates of their copolymers. Caprolactone moieties degrade faster than lactide units instead of their hydrophilicities are in opposite order. Elasticity of polymer maintain in hydrolytic degradation. Increase of caprolactone contents increase aging sensitivity and degradation temperature range. During the aging process a double T_g behaviour can be seen due to phase separation and crystallization of lactides. [17; 20; 25; 58]

2.1.4 Poly(glycolic acid) and poly(glycolic acid-co-lactic acid)

Poly(glycolic acid), PGA, is a simplest linear aliphatic polyester. Chemical structure is presented in Figure 2.3. PGA is highly crystalline, rigid polymer, with crystallinity degree of 45 – 55 %. PGA has glass transition temperature of 35 – 40 °C and high melting temperature, over 200 °C. Tensile strength vary between 60-100 MPa and ultimate elongation is 1.5 – 20 %. The modulus of elongation is around 5 – 7 GPa. PGA can be produced into self reinforced form which is stiffer and can have the modulus in range of 12.5 GPa. [33; 53]



$$\left[-CH_2-\underset{\parallel}{\overset{}{C}}-O-\right]_n$$

Figure 2.3: Chemical structure of polyglycolide. [33]

High crystallinity and high melting temperatures makes processing of PGA difficult. PGA can be dissolved into only couple of organic solvents, like hexafluoroisopropanol. Solubility can be improved by copolymerizing PGA with e. g. L-lactide or DL-lactide. PGA undergoes hydrolytic degradation and the strength is reduced in 1-2 months when complete degradation takes 6-12 months. Mechanical properties and degradation properties can also be modified by copolymerization. PDLGA 50/50 which is a copolymer of DL-lactide and glycolid acid is very sensitive to hydrolytic degradation. T_g, is around $40 - 50\,°C$. Tensile strength is approximately $41.4 - 55.2$ MPa and elongation vary between $2 - 10$ %. The modulus of elasticity is around 1-4.3 GPa. Degradation takes 1-2 months. An increase of DL-content, increase glass transition temperature and improves the resistance to degradation. T_g of PDLGA 75/25 is $50 - 55\,°C$ and the modulus to $1.4 - 4.1$ GPa while tensile strength and value elongation are in range of PDLGA 50/50. Degradation time is 4-5 months. [33; 53]

As a summary properties of biodegradable thermoplastic polymers, PLLA, PDLLA, PCL and PGA, are presented in the Table 2.1. Values or value ranges reflecting mechanical properties as well as melting properties of polymers are collected into the table.

Table 2.1: *Properties of PLLA, PDLLA, PCL and PGA. [22; 33; 53; 58]*

	PLLA	**PDLLA**	**PCL**	**PGA**
Crystallinity	crystalline	amorphous	semi-crystalline	semi-crystalline
Melting temperature (°C)	$175 - 180$	-	$55 - 60$	$224 - 226$
Glass transition temperature (°C)	$60 - 65$	$50 - 60$	-60	$35 - 40$
Tensile strength (MPa)	$15.5 - 150$	$27.6 - 50$	$20.7 - 42$	$60 - 100$
Modulus of elasticity (GPa)	4.8	1.9	$0.2 - 0.4$	12.5
Density (g/cm^3)	$1.24 - 1.30$	$1.25 - 1.27$	$1.11 - 1.146$	$1.50 - 1.71$
Degradation time (months)	$30 - 60, 7$	$12 - 16$	$24 - 36$	$6 - 12$

2.2 Manufacturing of nanofibers and nanofibrous scaffolds

A biopolymer sector includes different applications including fibers and textiles. In global textile field technical textiles is the fastest growing sector and it extends medical textiles, protective textiles and smart textiles. A big part of medical textile field encompass nanofibers and non-woven structures. Non-wovens are formed by bonding fibers mechanically or chemically into fabric form without converting them first into yarns. They are used e. g. in wound care applications and as scaffolds due to various controllable parameters like porosity, weight of fabric and thickness. [7; 8; 34; 42]

Nanoscale fibers and non-woven nanofibrous mats have increased demand in biomedical applications like in tissue engineering, biosensors, filtration, wound dressings and drug delivery. Nanofibrous materials are interesting alternatives in biomedical field due to high surface area to volume, low mass and small pore sizes but also good mechanical properties. In tissue engineering nanofibrous scaffolds have reported to promote positively cell-matrix and cell-cell interactions and enabling normal phenotypic shape and gene expression in cells. Fiber diameter scale is in same magnitude with fibrils of extracellular matrix and for that reason the nanofibrous material well mimic natural tissue environment and act as cell growth promoting substrate. [7; 34; 42]

Synthetic fibers are produced by delivering highly viscous liquid polymer through shape giving spinneret and solidified. In general fiber formation methods can be divided roughly into two groups, melt spinning methods and solution spinning methods, depending on how the polymer is formed into liquid form. The conventional fiber spinning method is melt spinning, in which polymer is melted under high temperature and pressure and fully melted polymer is extruded through a small die hole. The polymer is melted and pushed forward by pressure which is brought about with a spinning pump, e. g. with a extruder screw. The die hole can have various cross-sections and the diameter vary generally from 0.05 mm to 0.5 mm. Usually a ratio of the spinneret hole length to diameter vary between 2 to 10. Polymer chains partly orientate on the way through spinning nozzle and material is stretched. [31; 59]

Polymer melts are viscoelastic fluids which means that flow behaviour is a combination of irreversible viscous flow and reversible elastic deformation. The irreversible behaviour result from polymer chain slippage and the reversible behaviour is due to molecular entanglement. [19] Right after the polymer has exploit the spinning nozzle, elastic stresses of the polymer stream recovers and die swell occurs, which means the polymer stream expands. This is typical for viscoelastic materials and it is studied that the stream expands to 1.1-2.5 times the capillary diameter. Molecule chains are rather random orientation in as spun fibers. Spinning process is followed by fiber drawing, in which polymer chains are oriented and final fiber properties are created. Drawing is done at the temperature above glass transition temperature to achieve softening of amorphous parts of polymer and enhance the orientation of crystalline regions. A draw ratio affect properties of formed fibers. [19; 31]

The demand of polymeric nanofibers has highly increased in over past decade due to increase of number of possible applications and for that reason different nanofiber manufacturing methods has been developed. Nano- and microfibers are usually collected as nonwoven random fiber mats or nanowebs consisting of fibers with fiber diameters from several nanometers to hundreds of nanometers. The most studied and most common nanofiber forming method is electrospinning which is described in next section. The method has an edge over others due to possibility to fabricate continuous nanofibers and nanofibrous assemblies of various materials and control fiber fineness, surface morphology, orientation and cross-sectional configuration. As a disadvantage, polymers have to be dissolved and commonly used solvents are usually harmful. Some nano- and microfiber fabrication methods are potential compared to electrospinning and they can have an edge on electrospinning e. g. in scaffold manufacturing applications. [7; 34] Rotational melt spinning is one of these and it is studied more carefully in this work. But among these two, other methods are briefly presented in this study.

Meltblowing is simple one step method to produce micrometer or smaller sized fibers from melt-spinnable polymers. Molten polymer is extruded through a small orifice and stretched after that by air-drag. The air-assisted elongation can be done using cold or hot air flow parallel to extruded fibers. The orifice hole is reported to be around 0.1 mm and the velocity of the air flow within the range of 170-270 m/s. Fibers are collected onto collector as a web. Fiber diameter is influenced by throughput rate, melt viscosity, melt temperature, air temperature, and air velocity. Problems of this method are high melt viscosity of polymers and inability to produce orifice which is small enough. This method result to fiber diameters with fluctuation. [14; 34; 56]

Flash-spinning is a method to produce film-fibril strands from the solution of the polymer and liquid spin agent. The agent enables forming of a solution at high temperature or under high pressure. The spinning temperature is higher than the melting point of the polymer and the solution is spun into a condition of lower temperature or substantially lower pressure. This process is suitable for polymers which are difficult to be dissolved like high molecular weight polymers. The product is a non-woven fibrous web with wide fiber diameter range. [34; 51]

Bicomponent spinning is a two step process. The first step is to form bicomponent fibers by spinning two polymers through the die at the same time. The second step is to remove the other component from the fiber for example by dissolving it. Bicomponent fibers can have different cross-sectional geometries like island-in-sea, side-by-side, sheath and core or segmented pie structure. The geometry determines the shape of the formed unicomponent fibers. The problem of this process is to produce bicomponent fibers in micrometer scale. [34; 44; 56]

In a phase separation homogeneous polymer solution at required concentration is first refrigerated at gelation temperature and after that the gel is immersed in distilled water. The immersion induces solvent exchanging which is followed by removal from distilled water and blotting with filter paper and transferring to a freeze-drying vessel where nanofiber matrix is formed. This method is suitable only to laboratory scale production. [34] The last fabrication method is drawing which is a low productivity method where millimetric droplet of polymeric solution is placed on a silicon dioxide surface. After partial evaporation of solvent a droplet is touched by the edge of a micropipette and a nanofiber is withdrawn from the droplet. Nonuniform fibers are produced by this method. [34; 61]

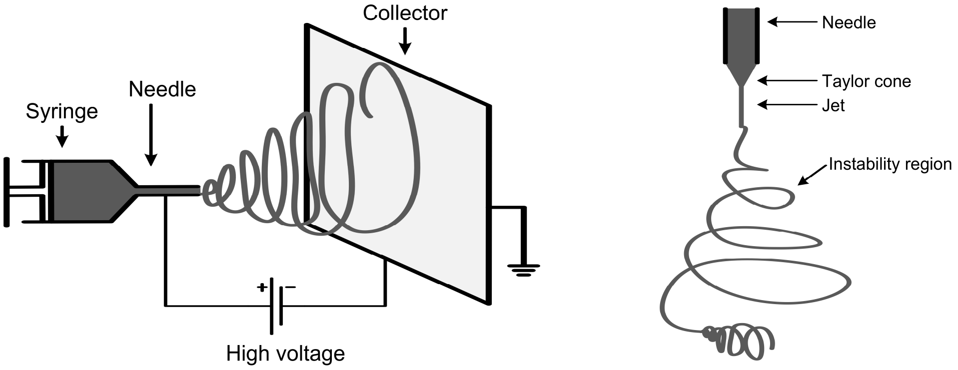
2.2.1 Electrospinning

Electrospinning is a method for producing submicron and nano scale fibers or fiber meshes usually from polymer solution but also from polymer melts. In this method charged polymer solution is transformed into a jet form and stretched to thin fibers using electric field. The mass production rate is slow but it is possible to produce fibers constantly and reproducibly by this method. [10; 27] The method is invented already in 1930s and the first patent was published in 1934 [7; 48]. Since that electrospinning has become common and widely investigated nanofiber forming method and the number of different patents is already approximately 50 [7; 10].

Electrospinning method and apparatus

The common electrospinning equipment consist of a glass syringe with polymer solution, a metallic fiber collector plate and a high voltage power supply. [27] The electric field is introduced between the syringe and the collector plate which can be located horizontally or vertically [7; 27]. Electric field causes the the transformation of the solution into a fiber form. [27] Electrospinning process can be divided in a confined feed system (CFS) and an unconfined feed system (UFS) processes depending on how the polymer solution is dispensed. In UFS processes the polymer feeding is unconfined and it can be caused for example by gravity. CFS is more common method and in that process the polymer solution is fed at constant speed. CFS can be further divided in four groups: a single needle electrospinning, multi-jets from single needle, multi-jets from multiple needle and multi-jets from needless system. [34]

The single needle electrospinning process is a traditional process and it requires two steps. At the beginning the polymer is dissolved into a solvent to get it into a liquid form and make it conductive [7]. After that the solution is placed in the syringe and pumped through a small charged needle at constant pressure [16]. Polymer solution get charged while going through the needle which is charged to 20-30 kV and forms a small droplet at the needle tip [10; 16]. The droplet is deformed into a conical shape called Taylor cone when it is under electric field but the surface tension of the solution is dominant. After the strength of the electric field between the syringe and the collector plate has overcome the surface tension of the droplet, a deformation of the droplet occurs and it transforms into a jet form [27]. The jet travels short distance stably and after that the interaction between electrical, surface and molecular forces becomes unstable which causes a bending of the jet into a form of an expanding coil. [10] Electrical bending instabilities results stretching of the jet and at the same time the solvent evaporates from fibers. [27]



(a) (b)

Figure 2.4: *(A) A schematic presentation of horizontal electrospinning process. (B) A close-up of electrospinning jet and different parts of it, a conical shape droplet called Taylor cone, stable straight jet, instability region of the jet.*

The productivity of single-jet from single needle electrospinning is low. To increase productivity the method has been developed further to form multiple jets from single needle. This multi-jet system is based on jet-splitting which can be carried out by using significant discrepancy in electric field distribution or by blocking part of the needle tip and split the jet mechanically. The discrepancy in electric field distribution can be achieved by applying axial electric field between the needle and the collector or just use a curved collector. [34]

Multiple jets can also be formed by using several needles. Needle configuration, number of needles and needle size are important factors in multiple needle system. Needles can be arranged in different configurations like linear or two dimensional shapes. Practical studies have shown that elliptical configuration is the best in case of productivity and process stability. In multi-jet system the behaviour of central jets and border jets might differ from each other and if needles are too close to each other, polymer jets can repulse each other and even block the action of central needles. Jet drying is also a problem in multiple needle system because central jets might still contain solvent when ending up to the collector. [34]

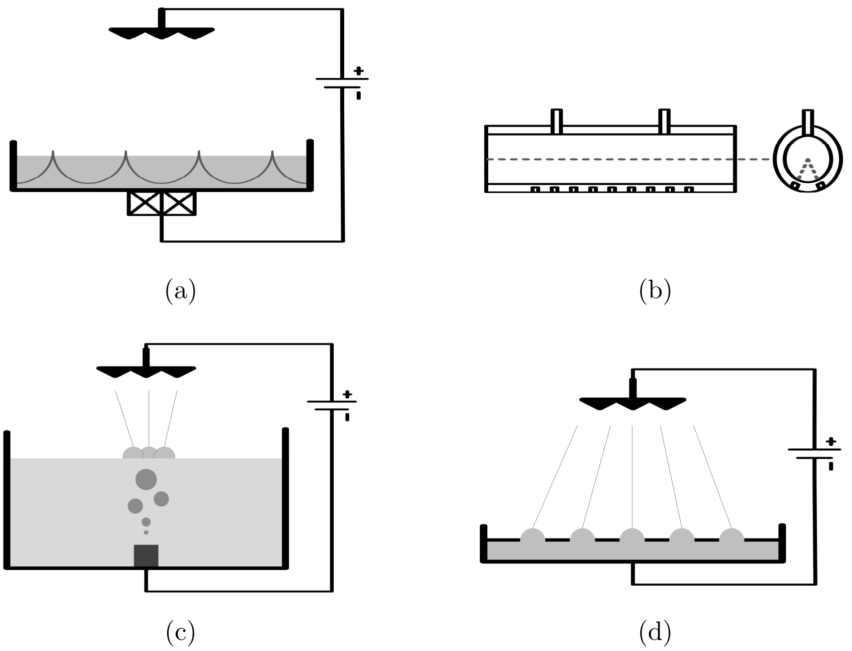
Complexity of the process, needle clogging and low productivity are problems of electrospinning method and new variations has been developed to overcome those problems. Most of these variations, like needleless electrospinning, bubble electrospinning, electroblowing and hollow tube electrospinning, include in the group of

UFS where the polymer feeding is unconfined. These multiple jet electrospinning methods produce fibers with larger diameter than single jet method. In needleless electrospinning the conductive polymer solution film is selforganized locally in mesoscopic scale in the impact of the applied electric field. Multiple jets are launched from the film when the voltage exceed the critical value. Higher voltage is needed than in nozzle techniques. The spinneret used in this method can be a metallic slowly rotating horizontal cylinder or a conical metal wire coil. Needles electrospinning is presented in Figure 2.5(a). [10; 34]

At Univestity of Akron, US, has been developed three different methods which are based on creating multiple jets instead of one jet. In hollow tube electrospinning process the needle is replaced by a hollow porous tube and multiple jets are created by drilling several holes on the surface of the hollow tube, presented in Figure 2.5(b). Production rates can be changed easily by varying the tube length and number of holes on it. In bubble launched electrospinning method a gas bubble is used to curve liquid polymer in a shape of a droplet surface and a polymer jet is launched from the top of the the polymeric bubble. A polymer liquid is inside a vertical cylinder and gas bubbles are introduced at the bottom of the reservoir by forcing the pressurised gas through a small tube. Gas bubbles rise up to the surface and create the polymer bubbles. One spinning jet is formed from one bubble but many bubbles can be formed same time which leads forming of multiple jets. The bubble launched electrospinning is presented in Figure 2.5(c). In blown polymer film electrospinning, polymer solution is formed into a film form and spinning jets are launched from it. A metallic wire mesh drum is partly put under a polymer solution and it is rotating on its axis and the polymer film is formed on the it. Air blown is channelled inside the drum and it stretch and curve the film across the openings of the mesh. Jets are launched from the apex of the curved film. This method is presented in Figure 2.5(d). [10; 54]

A large production scale SCF electrospinning method combines electrospinning and centrifugal spinning techniques due to the spinning syringe of an electrospinning apparatus is replaced by a rotating spinning disk. Electric field is applied between the rotating disk and a collector. A polymer solution is pumped in the middle of the disk and a rotation moves the solution to the rim where the surface tension of the solution breaks due to centrifugal force and multiple jets are launched. Liquid jets stretch and dry before reaching the collector plate. Polymer concentration and electric field strength have influence in forming fibers but rotation speed and ambient conditions have not an effect. The rotation speed was 6300 rpm and a voltage of electric field was 100 kV. The fiber diameter distribution is wide. [18]

Melt electrospinning can be a good alternative to polymers do not dissolve properly. It is much more rare to use polymer melts than solutions in electrospinning



(a) (b)

(c) (d)

Figure 2.5: *Different electrospinning methods, modified from [10]. (A) Needleless electrospinning process where polymer jets are launched from polymeric film. (B) Porous hollow tube electrospinning where needle is replaced by hollow tube with multiple openings. (C) Bubble launched electrospinning where gas bubbles are used to curve the surface of polymer solution and spinning jets are launched from it. (D) Electroblowing where polymer solution film is curved across the openings of metallic mesh and spinning jets are launched from the top of curved film.*

process. Spun fibers and non-woven felts produced by this method are relatively thick and that is why solution electrospinning has become more popular than melt electrospinning. High temperatures may cause degradation of polymers which also reduces utilization of the method. Heating temperatures vary depending on used polymers but at least temperature range from 90 °C to 320 °C has been studied. An applied voltage has been at same level than in solution electrospinning process and the collector distance depend on the melting of the polymer and the process temperature. High melting point polymers the collector distance was shorter, about 4 cm, and for low melting point polymers the distance was longer, 10 cm. In melt electrospinning process fibers should have time to cool but with that fibers melt together when collected in many studies. [7; 12]

A collector is critical in fiber forming process and different collector types exist. The chosen collector type affect the controlling of fiber orientation and position of them. In a lithographic technique fibers are spun into a resist mask from where the pattern usually need to transfer into material of the choice. In the direct deposition of electrospun fibers, there is no need to transfer the fibers afterwards and fibers can be directed in mechanical or electrical way. Mechanical direction means that the collector can be stationary or in motion. The motion can be rotary or oscillatory motion. Rotating drums or wheels are usually used when aligned fibers are wanted. Collecting of straight fiber segment is possible when sample moves at the same speed as fiber is deposited from spinning tip. In general the linear stage motion is not fast enough to allow the sample move at the same speed than fibers are deposited which results to formation of 2D-patterns. One way to direct fibers electrically and form patterned areas is to use electrodes behind the collection areas. It is also possible to modify the electric field between the tip and the grounded collecting substrate and focusing it by electrostatic lens or time-varying electric field. Instead of one electrode as a collector it is possible to use two separate grounded electrodes to produce aligned mat. Electrospinning jet jumps back and forth between these two electrodes and the technique can be used to produce even more complex but controlled patterns. Spaced ring electrodes are used to produce suspended aligned fibers which can be then twisted to form fibers. [4]

Parameters affecting electrospinning

Process parameters which have an influence in morphology and moreover in properties of formed fibers can be divided in three groups: solution parameters, process parameters and ambient parameters. These are presented more detailed below. Solution parameters reflect rheological and electrical properties of solution and they consist of viscosity, molecular weight, surface tension and conductivity. Viscosity is a measure which reflects fluidal properties of liquid and a resistance of it to change shape. The viscosity is related to the concentration of the solution which affect the surface tension of the solution and finally has influence in a diameter and a morphology of forming fibers. Optimal solution concentration is also crucial for spinning process because fiber forming is not possible if the viscosity is too low or too high. Low concentration leads to formation of polymeric beads instead of continuous fibers and high concentration leads to formation of thick fibers. The solution concentration leads to increase of fiber diameter. Molecular weight also has an influence in a viscosity of the solution. Molecular weight of the polymer correlate the size or the length of polymer chains. It affects rheological and electrical properties of the solution and impact in the surface tension. Among these it affect conductivity and dielectric forces in solution. [7; 34]

Among the viscosity, the surface tension and conductivity are critical solution parameters in fiber forming process. Surface tension determines the strength of electric field needed and the shape of forming product. Low surface tension enables the electrospinning process at lower electric field than high surface tension. Too high surface tension leads also formation of beads instead of fibers. Low surface tension is then more desired and the surface tension can not be too low. It is possible to impact on surface tension via composition of the solvent. Conductivity can be defined as surface charge density and it affect the easiness of spinning. When the conductivity is too low, the spinning jet does not elongate enough and fibers are not formed. Polymer type and solvent but also the availability of ionisable salts in the solution affect the conductivity. [7; 34]

Process parameters include strength of applied electric field, a collector type and a distance between the collector and a spinning tip but also feeding and flow rate. Electric field is formed by applying voltage between a spinning syringe and a collector plate. Induced charges are necessary to initiate the electrospinning process. In most cases an increased applied voltage results to decrease of fiber diameter but there are also some research results which shows that electric field has no effect. A type of a metallic fiber collector vary depending on the desired final product. In general an aluminium foil is used as collector but the problem of it is the difficulty to transfer collected fibers. Different collectors are needed when aligned, continuous or parallel, fibers are wanted. Conductive paper or cloth, wire mesh, pin, rotating rod, parallel or grided bars and coagulation bath are widely used. Surface area of conductive collector material and the distance between the collector and the syringe are critical parameters in fiber forming process. The collector distance should be long enough so that fibers are able to dry before reaching it. Among the collector distance a flow rate of polymer from syringe affect drying. Lower feed rate gives more time for solvent to evaporate. In some cases collector distance has also effect on the fiber cross section so that short distance leads to flatter fibers and longer distance to round shaped fibers. If the collector is too close or too far, beads are formed. Bead formation is also possible if the conductive area of collector is too small. [4; 7; 34]

Ambient parameters like humidity and surrounding temperature have been studied. Electrospinning process can be carried out in room temperature but increased surrounding temperature lower the viscosity of polymer solution which causes a decrease of fiber diameter. Temperature studies have been done in temperature range of $25 - 60\,^{\circ}\mathrm{C}$. In fiber forming process solvent evaporates from fibers and for that reason good ventilation system is required. Usually the process has done in fume chamber. Humidity affect the evaporation of solvent from spun fibers. Too high humidity causes small circular pores to the surface of fibers and if the humidity increase more, pores will combine. Low humidity can cause too fast evaporation of solvent which can lead to clogging of the syringe. [7]

Electrospun products

Electrospun products are nanofibers or nanofibrous assemblies from various materials with low enough viscosity. The method enables to control properties of forming fibers like finess, surface morphology, orientation and cross-sectional configuration. Usually electrospun fibers are smooth and they have constant fiber diameter, but also beads-on-string like fibers can be fabricated. Fibers with diameters less than 100 nm can be manufactured but usually melt electrospun fibers are thicker. Electrospinning enables fabrication of solid and hollow fibers as well as fibers with coaxial inhomogeneity, like fibers with side-by-side morphology. End-products can be randomly orientated fibers, aligned non-woven mats, isolated nanofibers or fibers which are deposited in controlled pattern or predetermined locations. The geometrical shape of end-product vary depending on the collector. E. g. flat and tubular products can be produced. Non-woven products have high surface area, high porosity compared to the mass and small pore size. A production rate is slow, approximately 0.3 g/h. Electrospun fibers may be dissipated or retained by electrostatic charges depending on electrical properties of the polymer and fibers can be manipulated afterwards by electrical field or voltage. Electrospinning process is suitable processing technique to many synthetic and natural polymers but the spinning of very viscous fibers do not succeed. One or the other of polymer and solvent should be electrically conductive. Numerous biodegradable polymers like poly-ε-caprolactone (PCL), polylactides (PLAs), polyglycolides (PGA), polyurethane (PU) and copolymers like poly(lactide-co-glycolide) (PLGA) and the poly(L-lactide-co-ε-caprolactone)(PLCL) are reported to be able to spin by electrospinning. [4; 7; 32; 34]

2.2.2 Rotational spinning

Rotational spinning is a high throughput method for producing submicron scale fibers and fiber meshes using centrifugal forces. Polymer is got into a liquid form usually by melting, but in some cases by dissolving, and spun to fibers using high speed rotation. This is quite novel method to produce textile fibers but the original idea of heating and transforming the material into filaments using rotation is already presented in 1899 when a cotton candy machine has been invented. Rotational melt spinning is studied less than electrospinning as a processing method of polymers and at the moment limited number of publications exist. So far the technique has shown to be promising method to produce submicron scale fibers without using any solvents or electrical forces. Other advances are a high throughput rate and possibility to produce 3D-structures. For these reasons researchers have become interested in rotational melt spinning technique. [2; 23; 47]

Rotational melt spinning method and apparatus

In rotational spinning technique a material is transformed into a liquid and after that spun into a filament form using centrifugal forces. A rotational spinning apparatus contain a spinneret which rotate about its axis, usually a heating element and a collector. The spinneret contain a reservoir for material and openings for an

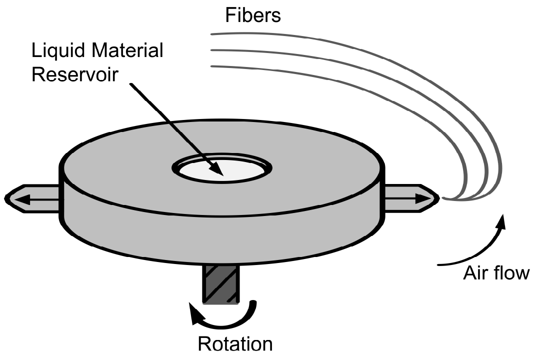
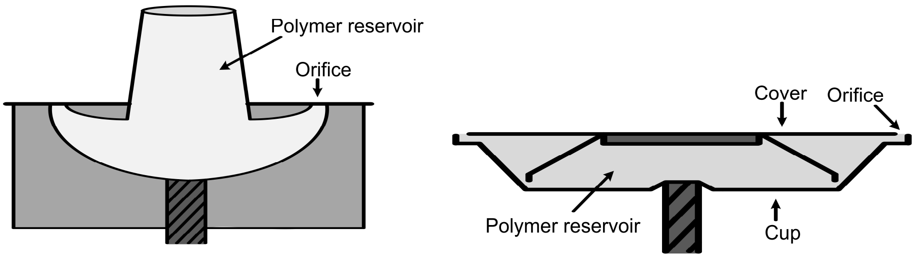


Figure 2.6: *Rotational spinning method, modified from [37].*

output of the material. The centrifugal forces promote fiber forming by pushing the liquid polymer through the orifices of the spinneret and causing the formation of a polymer jet. While the centrifugal force promote the fiber forming process, the surface tension of the jet resist it and the whole fiber forming process is based on competing of these two forces. Thermo-flow polymer stream exploits the spinning nozzle at high speed and polymer chains elongate due to air flow before a solidification of the polymer stream. Rotational spinning technique is presented in Figure 2.6. Rotational spinning and the fiber forming process has been investigated using different cotton candy machines, but also using devices which are designed for the purpose. Both, solution spinning and melt spinning, has been studied but the solvent free melt spinning is more desired in many applications and that is why a promising alternative for electrospinning. [2; 50]

The design of the spinneret can vary depending on the material under processing. Here are presented different spinneret types which are studied in literature. Two spinnerets which are commonly used in commercial cotton candy machines are defined already in early patents in the end of 19$^{\text{th}}$ century and in the beginning of 20$^{\text{th}}$ century. The first type of spinneret consist of a cup and a cover with an annular opening between them. The heater is placed under the cup. Material is put inside the cup and heat up there. After melting the polymer is directed through a narrow gap between the cup and the cover and transformed into a fibrous form. In Figure 2.7(a) is presented the very first spinneret of cotton candy machines and in the Figure 2.7(b) is a later design of the same spinneret. [46; 47]

The second type of spinneret is presented in patents of a spinneret of a cotton candy machine and a spinneret of an apparatus for transforming the physical structure of thermo-flow materials. The spinneret consist of a round shape orifice band with multiple openings placed between a bottom plate and a cover. An annular heater element is placed inside the orifice band in close proximity of it. The thermo-flow material is put as in solid form into a spinneret and it is centrifuged against

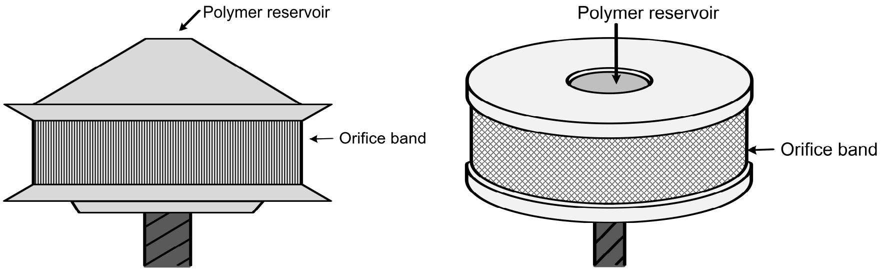


(a) (b)

Figure 2.7: *Cup and cover shape spinnerets with annular openings. (A) Design of the spinneret from very first cotton candy machine, modified from [46]. (B) More modern design of cup and cover spinneret, modified from [49]*

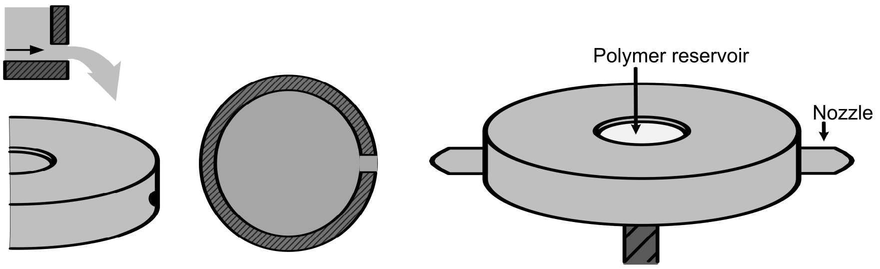
the heating element. After melting, the material is directed through holes of the orifice band and transformed into a fibrous form. Openings of the orifice band can differ from round circular openings to long cuts. In Figures 2.8(a) and 2.8(b) are presented spinnerets with two different kind of orifice bands. [47; 50]

There are also spinnerets which are designed only for processing of polymers. One of these is a cylindrical rotating reservoir with only few side wall orifices, presented in Figure 2.9(b). The wall thickness is higher than the thickness of the orifice band which is presented above, so the ratio of orifice length to diameter is higher than in case of the orifice band spinneret. Typically the wall thickness is a few millimeters and orifices with diameters around 0.3 mm are in the wall. [2] A little modified version, a spinneret which is assembled from plates, combines ideas of the syringe and the cylindrical side wall spinneret. The assembled plate spinneret contain a reservoir and long wall orifices. The spinneret is built up at least a top plate and a bottom plate and it includes multiple long nozzles as orifices. The nozzles are long grooves from the middle of one plate to the ring of it. In the middle of a spinneret is polymer reservoir where the material can be placed in solid or in liquid form. Last



(a) (b)

Figure 2.8: *Orifice band spinnerets, modified from [47]. (A) Design of orifice band spinneret with long vertical cut openings. (B) Design of orifice band spinneret with web orifice band.*



(a) (b)

Figure 2.9: *Spinnerets designed for processing of polymers. (A) Cylindrical polymer reservoir with side wall orifices, modified from [2]. (B) Polymer reservoir with small nozzles as openings, modified from [37]*

spinneret option which is presented in literature is a horizontally set syringe with a needle as an opening. [52]

In case of all spinnerets above, the polymer is extruded through the orifice or orifices. Polymer flow varies when melted polymer is extruded through the capillary. External forces, centrifugal forces in case of RMS, push the polymer melt forward but the capillary causes additional stress to the polymer melt. Intensity of formed stresses depend on rheology of the polymer melt. The polymer melt flow can be divided in four flow zones depending on capillary stage. The first zone is low-shear zone where capillary walls do not cause high external stress to the polymer stream. The second zone takes place when the polymer stream near the inlet of the capillary and shear stress increases. The third zone exist in the capillary where shear rate is high but shear stress decreases. Constant flow characteristics exist in this zone. Polymer chains try to orientate among the capillary when the polymer melt flow through it. Dimensions of the capillary determine the amount of elastic strain relaxation which occurs. Dimensions have also influence in the onset of instabilities of the flow, like melt fracture and draw resonance. The last zone takes place when the polymer emerges from the capillary. Shear rate and shear stress decrease rapidly, the melt cools causing increase of apparent viscosity and stored elastic energy releases. This causes swelling of polymer stream. [35; 31]

The diameter of spinneret, others than the syringe type, is typically 3-8 inches (7-20 cm) and the high of the spinneret is 1-2 inches (2,5-5 cm). Openings are quite often straight hole with circular shape cross-section with diameter varying from 0.01 mm to 1-3 mm. Length of the openings is typically from 1-3 mm to several centimeters. The optimal ratio of orifice length to diameter is studied to be 2-10. A geometry of the spinneret also affect the feeding of the material. The polymer can be fed continuously during the spinning process or it can be placed once inside the spinneret in the beginning of the process. In a batch process the polymer is not added during the process and the spinneret can be open from the top or the the polymer reservoir can be closed like that the spinning nozzles are the only openings. The polymer can be added in granule form or as a solution. The continuous polymer feeding requires the spinneret where is an open hole on the top of the spinneret. Polymer can be in solid or pre-melted form. The polymer feeding rate has an influence in the fiber forming rate which is around 1 g/min. [2; 32; 52]

Among a spinneret the rotational spinning apparatus contain a heating element and a motor to rotate the spinneret and a collector. Both resistance and inductance heaters exist and there are variable controlling systems for heating and rotation depending on an apparatus. The heating system can be in direct contact with the spinneret or it can be placed for a distance depending on the chosen spinneret. Usually resistors, tube resistor or plate resistor, are in direct contact with the spinneret. IR-heaters and ovens can be used for distance. Depending on the machine the heating system can be independently adjustable or it can be coupled to the rotation. The heating and temperature adjustment can occur before spinning, during the spinning or both before and during the spinning. When the polymer is melt during the rotation, higher temperatures and longer processing times might needed. This may lead the degrading of polymer chains. Typical processing temperature range is from 4 °C to 400 °C but extreme temperatures like from −20 °C to 1500 °C is able to use. After spinning fibers can let cool in process of time but also air helped cooling is able to use. A spinning speed can be adjustable. The rotation speed can vary usually from few thousands turns per minute (3000-5000 rpm) up to several thousands turns per minute (12,000 or even 25,000 rpm). The rotation might start at high speed in the beginning or there can be a slow motion area so that the rotation speed accelerates before reaching a high speed. During the spinning the rotation speed can be fixed or adjustable [2; 52].

Different fiber collection methods exist. Collector bowls, collector walls and parallel collector rods placed in circular shape around the spinneret are reported to be used. Fibers are collected in interior of the collection wall. An intermediate wall can be placed outside of the collector wall. The function of the intermediate wall is to affect the air flow caused by the spinneret and to ease the collection of fibers. The air flow is controlled by changing the height or the diameter of the intermediate wall. Also external air flow can be used for directing fibers in desired direction. Low-pressure conditions and high-pressure conditions brought by vacuum pump or pressure pump can be used to direct fibers. Collection rod or several of them are used to collect fibers. The rod can be rotated about its axis and the fibrous floss can be whirled around it during the collection. The rotation speed of collection rod vary between 50-250 rpm. [2; 23; 52]

Rotational melt spinning is quite novel fiber spinning method and small number of research groups are studied it. Here is shortly presented current research studies.

At Harvard University rotational spinning has been studied using polymer solutions and a spinneret with side wall orifices, like in Figure 2.9(b). The process is called rotational jet spinning, RJS. The research group has studied the effect on the rotation speed and the jet surface tension on fiber forming. Investigated rotation speeds has been from 4000 rpm to 12,000 rpm and constant polymer feeding has used. [2] At Tampere University of Technology rotational melt spinning has been studied using two commercial cotton candy machines having different spinnerets. The effect of inherent viscosity (iv) of the polymer on spinning process is evaluated in the studies. [23; 29] In collaboration of Kyoto University, Japan, and Ecole Normale Supérieure, France, has been investigated rotational melt spinning for preparation of polymeric fiber scaffolds for cell culture studies. The process is called centrifugal melt spinning (CMS). The studies are done using two commercial cotton candy machines with a rotation speed of a few thousand turns per minute and an adjustable heating temperature within the range of $50-200\,^{\circ}\mathrm{C}$. Low glass transition temperature polymers, rotation speed and heating temperature has been studied. [55] At University of Texas Pan American in Texas the rotational spinning has studied using polymer solutions and melts. The technique is called Forcespinning$^{\mathrm{TM}}$. Research studies are done with their own spinning device with multiple different changeable spinnerets and with a rotational speed at least up to 12,000 rpm. The spinnerets are designed for polymeric materials and they are assembled from plates. The thermal system makes it possible to control the heating and the cooling process. Spinneret and nozzle configuration, orifice size, rheological properties of polymer, rotational speed and temperature are all studied to affect the morphology of forming fibers. Research studies has lead an incorporation of a company called FibeRio® Technology. [37; 39]

Rotational melt spinning parameters

Parameters which affect the fiber forming by rotational melt spinning and end products can be divided in process parameters, polymer parameters and ambient parameters. Process parameters include a device configuration, a rotation speed, a heating and cooling method and polymer feeding. A device configuration includes geometry of a spinneret and nozzles, a collector type and design of rotation and heating elements. Different spinnerets are presented above and the spinneret type affect the way how fibers are formed but also the size and morphology of them. Cross-sectional shape and diameter of openings determines the cross-section and thickness of forming fibers. Also the angle of the openings along with rotation speed and processing temperature affect the fiber thickness and cross-section. The optimal ratio of orifice length to diameter has been studied to be 2-10. Irregularities in nozzles cause formation of fibers with wide range in diameter. The spinneret define how the polymer can be fed or placed into a reservoir. In case of a batch process the polymer is placed into a reservoir in the beginning of the process and it flows out at own rate. The controlled rate of polymer outcome can be achieved by continuous feeding of polymer. The feeding method has an influence in the fiber forming rate and in morphology of formed fibers. Controlled, continuous material feeding may lead controlled end-products. [2; 23; 31; 52]

Elevated processing temperature is required in melt spinning process to liquefied the polymer. The processing temperature depends on the glasstransition and melting temperature of the polymer under processing. Rapid and efficient heating is desired. Due to effect of elevated temperature and time on polymer, a short processing time is ideal. The shorter the processing time is, the less harm it causes to the polymer. Processing time and temperature are dependent on each other but also on the spinnable material. Higher molecular weight polymers usually need higher processing temperatures. When the polymer is melted during the rotation, higher temperatures and longer processing times might needed. This may lead the degradations of polymer chains. The heating temperature affect properties of polymer melt, like viscosity. Lack of temperature control leads the wide range of fiber diameter. Among the heating temperature the cooling temperature has also important role in fiber forming. Too quick cooling reduces sufficient stretching of fibers and too slow cooling leads to welding and bunching of fibers due to they touch each other before solidification. [23; 52]

Rotation speed is related to the centrifugal force which is a pushing force in fiber forming process. The centrifugal force increases at higher rotation speed. Higher centrifugal force leads to higher extension of stream and thinning of the jet when lower rotation speed leads to thicker fibers and wider distribution in fiber diameter. [2; 23] Too low speed lead to formation of quite thick fibers and beads. Too high spinning speed lead binding of the fibers and forming of fiber clusters. This means that an optimal spinning speed exist. [55] High molecular weight polymers need higher rotation speed than smaller molecular weight polymers. High rotation speed result to smaller fiber diameter variation than low rotation speed which means that a standard deviation in fiber diameters is lower [32]. A long collector radius let fibers flow freely and that leads continuous and aligned fibers. A short collector radius leads to nested and blended fibrous structures. [23] The temperature of collection wall may increase over ambient temperature and that may hamper collecting of fibers. Fiber bundling or welding is possible but it can be controlled by blowing gas to decrease the temperature. For example air and nitrogen can be used. [52]

Polymer parameters which affect on liquefaction and rheological properties of polymer liquid are crucial. In case of melt spinning suitable melting point and correctly selected molecular weight are required. When using solvents dissolving of polymer is required. The concentration of polymer solution used in rotational spinning must be higher than the solution used in electrospinning process. Also spinning of non-conductive liquids is possible unlike in electrospinning. [23; 39] Molecular weight is an important polymer parameter and it affect the properties of solution or melt, like inherent viscosity (iv) and surface tension [2; 23]. Inherent viscosity is a viscometric tool for evaluating molecular size of polymer and it correlates flow properties of polymer. Inherent viscosity value is determined from solution by comparing of the flow time of the solution through a narrow capillary to the flow time of pure solvent. It also can be determined as a ratio of natural logarithm of relative viscosity to the plastic concentration where the relative viscosity is the ratio of viscosity of the solution to the viscosity of the solvent [38; 45]. The unit of inherent viscosity is dl/g and the determination of iv is presented in equation 2.1.

$$IV = \eta_i = \frac{ln\eta_r}{c} = \frac{\frac{\eta}{\eta_0}}{c} \qquad [\mathrm{dl/g}] \tag{2.1}$$

Lower iv-value relates to lower melt viscosity. The lower melt viscosity enables processing in lower temperatures which restrain polymer degradation. Rotational melt spinning has been studied using different molecular size polymers with high and low iv values. Studies were made with rotation speed of few thousands turns per minute. Those studies showed that quite low iv-value is the best for melt spinning process and the optimal iv-value would be approximately 0.8-1.2 dl/g. End-products vary depending on the iv-value of the polymer. High iv-polymers, iv of 5.16 dl/g, prevent the fiber formation and it produced flakes whereas low iv polymers, iv of 1.6 dl/g, are able to process into form of continuous fibrous floss. The observation of iv was made before and after the processing and the changes of molecular weight was studied. iv-values decreased during the processing but no monomer was created which means that the melt spinning process is robust enough. Inherent viscosity values decreased to values of 0.86-0.98 dl/g. [23; 36]

In fiber formation process a surface tension of the liquid or more detailed polymer stream resist the fiber formation. This causes a jet rupture and may lead to formation of droplets instead of fibers. The ratio of viscous force to surface tension force determines the level of the instability and also a probability of droplet formation. The instability cause thinner and thicker parts locally into a jet and the jet can breakup from thin places. This process is a Plateau-Rayleigh instability. It is assumed that the surface tension and the polymer concentration correlate together in case of polymer solutions. It is related to the polymer chain overlapping and entanglement. In case of too low concentration there is no entanglement of polymer chains and beads are formed. Increased polymer concentration, the value above a critical value, lead to sufficient chain entanglement and continuous fibers are formed without beads. Too high concentration results to too thick fibers. [2; 41]

The spinning process do not require any critical ambient conditions and it can be done in normal room conditions. Nevertheless, the spinning process is usually carried out in vacuum chamber with controlled ventilation system. The ventilation affect the stretching of fibers but also collecting of them. The rotating spinneret creates an air flow which is not always sufficient. The formed fibers can be directed to the collector using high pressure. The surrounding temperature affect the cooling rate of fibers and that way stretching of fibers too. Fiber cooling and solidification should occur before collection of them but on the other hand too quick cooling rate prevent stretching of them. In case of rotational melt spinning the humidity of air may cause unwanted hydrolytic degradation of polymers and use of protecting atmosphere may be justified. [2; 39; 52]

Rotational melt spun products

Centrifugal melt spinning is a rapid process to produce three dimensional fibrous structures with arbitrary shape. Fibrous structures like webs, meshes or mats can be produced when cross-links exist between fibers. Aligned fibers from the web can be further spun into yarns. Fiber diameters vary from micrometer scale to nanometer scale depending on the machine and process parameters but the fiber size distribution is not homogenous. Fiber lengths vary from millimeter range to centimeters and circular, elliptical or rectangular cross-sections can exist. The fiber morphology can be textured or smooth and fibers may be lumen or multi-lumen. Rapid extensional flow and fiber cooling may result to incomplete crystallisation. The material degree of crystallinity decreases during processing and the crystallinity of fibers is lower than the crystallinity of initial bulk material. The production rate is high, approximately 1 g/min. [2; 23; 32; 39; 52; 55]

Centrifugal melt spinning is suitable for thermoplastic polymers which have suitable melt viscosity. Different polymers with different machine modifications and different processing parameters are studied. High molecular weight polylactide (96L/4D) and low molecular weight lactide (50L/50D) has been used in centrifugal melt spinning trials. Studies were made with a cotton candy machine without any fine-tuned parameters. Rotation speed has been a few thousands turns per minute. Spinneret nozzle has been a narrow continuous cavity between two plates, a collector diameter of 60 cm and heating time has been approximately 3-5 min. High molecular weight PLA has high iv-value. The polymer transformed into flakes during the processing. The iv-value found out to be too high and it decreased from 5.16 dl/g to 0.98 dl/g. Low molecular weight PLA has low iv-value. The polymer transformed into a continuous fibrous floss with large fiber distribution range from 993 nm to 10-50 μm. The iv-value decreased from 1.6 dl/g to 0.86 dl/g and it was also too high for nanofiber formation. [23]

Poly-lactide-co-glycolide, PLGA, with different compositions has been studied using commercial cotton candy machines. PLGA 85/15 with molecular weight of 50,000-75,000 has been pre-heated up to 150 °C and spun out in 2 minutes using rotation speed of a few thousands turns per minute. The collector diameter was 80 cm. T_g of the material was $40-50$ °C. 1-10 μm sized fibers were able to spun but not fibers with less than sub-half micron size. [55] Other studies are made using poly (D, L-lactide-co-glycolide), PLDGA 70/30 and PLDGA 75/25. A rotation speed has been also a few thousands turns per minute. The temperature range has been $170-200$ °C or $215-220$ °C depending on the machine. Smallest fibers were at nanoscale and thicker fibers more than 50 μm. M_w PLDGA 70/30 change from 110 600 to 81 800. IV of raw material vary between 1.53-0.8 dl/g. [29]

Polystyrene (PS) has been processed by rotational melt spinning method. 30 grams of polymer has first melted in temperature range of $190-260$ °C and after that 30 ml of polymer melt has placed into a spinneret which is pre-heated up to 240 °C. The polymer has spun into fibers with different spinning speeds from 1000 to 6000 rpm. Best results were achieved using temperature of 240 °C and rotation speed of 4500 rpm. The spinning time was about three minutes. Same kind of test were done to other polymers too. Best results in processing of acrylonitrile butadiene styrene (ABS) were achieved by preheating the material in $210-280$ °C and after that spun in 280 °C and 4500 rpm. Most fibers were micron sized. Processing of polycarbonate in temperature of $300-350$ °C at rotation speed of 1000-5000 rpm produced also micro- to nanofibers. Nylon 6 and polypropylene (PP) were processed. Meltspinning of PP in 225 °C at 12 000 rpm took 30 seconds. Average fiber diameter was 372 ± 283 nm and small beads was found. Nylon average fiber diameter was 165 ± 55 nm. [37; 52]

2.2.3 Comparison between electrospinning and rotational melt spinning

Electrospinning and rotational melt spinning techniques are compared with each other based on literature review. Advantages and disadvantages as well as significant processing parameters are summarized in Table 2.2. In general, electrospinning is slow, expensive and complex method when rotational melt spinning is simpler method with high production rate. As a disadvantage of electrospinning, harmful solvents are used. On the other hand, the method enables fabrication of thinner fibers than rotational melt spinning. Among larger fiber diameters, rotational melt spun fibers have more fluctuation in fiber diameters when electrospinning result to constant fiber diameters.

Table 2.2: Summary table of electrospinning and rotational melt spinning.

	Electrospinning	**Rotational melt spinning**
Advantages	Uniform fibers, constant fiber diameter Possibility to control fiber fineness surface morphology, orientation and cross-sectional configuration of forming fibers Processing in room temperature Ability to fabricate continuous products	High production rate (1 g/min) Simple method No high voltage required
Disadvantages	Complex method Slow method Low productivity, (up to 300 mg/hr) Use of solvents Low fiber yield Use of high voltage power source	Elevated temperature Slightly thicker fibers
Parameters	Solution viscosity and surface tension Conductivity of solution Strength of electric field Collector type and distance Spinning tip Humidity and temperature	Spinneret and nozzle geometry Rotation speed Heating and cooling process Polymer melt viscosity Inherent viscosity Molecular weight
Products	Constant fiber diameter Continuous fibers Nanofibers	Aligned 3D structures Arbitrary shape Variable fiber diameters
Polymers	Soluble polymers	Low viscosity thermoplastics

AIMS OF THE WORK

- The main purpose of the work are to study rotational melt spinning technique as an alternative to electrospinning and find out critical processing parameters.

- The objective is to manufacture micron and sub-micron scale fibers or fiber mats for research studies via Cretors Ringmaster Lite.

- As a first objective is to modify the machine suitable for fabrication of micron and sub-micron scale fibers from biopolymers. The purpose is to determine possibilities to produce polymeric fibers via existing device and modify the machine and the spinneret so that they are suitable for processing of polymers. Any permanent changes to geometry of the machine are not desired.

- Determining suitable processing parameters for different polymers.

3. MATERIALS AND METHODS

Rotational melt spinning (RMS) and electrospinning of biopolymers are studied and process variables are presented in this chapter. Suitability and effects of different polymers on rotational melt spinning and electrospinning are investigated using polymers which belong to group of poly(α-hydroxy acids). Proper solution properties and processing parameters are examined in case of electrospinning. The study of rotational melt spinning consist of an experiment of the spinning device and modifications of it but also variations of processing parameters.

3.1 Polymers

3.1.1 Polymers and polymer solutions for electrospinning

Suitable polymers, solvents and material quantities of spinnable solutions are studied from literature review and electrospinning solutions are prepared among the review study. The viscosity of the solution is critical due to it has influence in the droplet formation on the tip of the needle which affect the succeeding of the process. Molar weight of polymer and concentration of the solution determine the viscosity of the solution. Polymer solution is prepared by dissolving polymer granules into the solvent and mixing the solution by magnetic stirrer in closed pot over 24 hours. Trifluoroacetic acid, TFA, is used as the solvent for all polymers. Spinning solutions are presented in Table 3.1.

P(L/DL)LA 70/30, poly-L,DL-lactide 70/30, has molecular weight M_w, of 180 kg/mol and iv-value of 3.1 dl/g according to manufacturer's information. Two batches of solution are prepared with concentrations of approximately 8 w-% and 9 w-%. Before spinning process solutions are stored in fridge. The first solution with concentration of 8 w-% was two weeks old when it was spun and the viscosity of the solution was already decreased due to too long storing time. The second solution with concentration of 9 w-% was spun right after preparation of the solution but the solution was contaminated. Some impurities detached from the lid of the bottle where the solution was stored.

Table 3.1: Polymers and polymer solutions for electrospinning.

Sample	Polymer M$_w$ (kg/mol) IV (dL/g)	Solvent	Polymer w-%	Age of solution	Notes
ES_PLDLA_70/30_1	180 3.1	TFA	approx. 8	2 weeks	
ES_PLDLA_70/30_2	180 3.1	TFA	approx. 9	1 day	Impurities
ES_PLGA_80/20	- 5.72	TFA	approx. 13	4 days	

PLGA 80/20, poly(L-lactide-co-glycolic acid), is purchased over ten years ago and it has stored in plastic bags in room conditions. The IV-value of the polymer is 5.72 dl/g according to measurements done in year 2001. A concentration of spinning solution is approximately 13 w-% and the solution was stored three days before spinning.

3.1.2 Polymers for rotational melt spinning

Four biodegradable melt processable polymers are studied. Polymers with varying iv-values and melting ranges are used to evaluate the effect of material to the spinning process. Polymer granules are dried and stored in a vacuum chamber after taking them out from the freezer, where polymers are stored first. In the vacuum polymers are stored in small batches, approximately 20 g of polymer in one plastic lidded pot. In the beginning of the processing polymer granules are in contact with air for a moment, when granules are placed into a reservoir of the spinneret. Nitrogen atmosphere is not able to use there. Following polymers are used and they are summarized in Table 3.2.

P(L/D)LA 96/4, poly(L-lactide-co-D-lactide) 96/4 is a semi-crystalline copolymer from Purac Biochem, Gorinchem, The Netherlands. It is medical grade polymer with high iv-value of 2.13 dl/g and melting range of 146.7-156.4 °C according to the manufacturer's data sheet. Granules are approximately 2-3 mm in diameter.

PDLA 50/50, poly-DL-lactide 50/50, is amorphous non-medical grade polymer from Purac Biochem, Gorinchem, The Netherlands. PDLA 50/50 has inherent viscosity of 1.52-1.53 dl/g and melting range of 52.9-54.6 °C. A granule size is in the order of the granule size of PLDLA 96/4.

Table 3.2: *Polymers used in rotational melt spinning.*

Polymer	Melting range,(°C)	iv,(dL/g)
P(L/D)LA 96/4	146.7-156.4	2.13
PDLA 50/50	52.9-54.6	1.52-1.53
PCL	58.2-60.0	1.06
PLCL 70/30	-	1.5-1.6

PCL, poly-ε-caprolactone is semi-crystalline non-medical grade polymer from Purac Biochem, Gorinchem, The Netherlands. iv-value of PCL is 1.06 dl/g and the melting range is 58.2-60.0 °C. Granules are small flakes and little bigger sized than PLDLA 96/4 granules, up to 5 mm in length.

PLCL 70/30, poly(L-lactide/ε-caprolactone) 70/30 is a copolymer from Purac Biochem, Gorinchem, The Netherlands. iv-value is in range of 1.5-1.6 dl/g. The granule size is little bigger than PLDLA 96/4.

3.2 Electrospinning

Electrospinning was done in the Department of Materials Science at Tampere University of Technology. Practical work was done by Johanna Laine using the device of the department as a part of hers master of science of work.

3.2.1 Electrospinning device

The electrospinning apparatus consist of a high voltage power supply, a glass syringe with a replaceable positively charged needle and a negatively charged collector plate made of copper. The right-angled shape glass syringe, volume of approximately 5 ml, is placed to a holder and a metallic needle is attached to the syringe. The device do not contain a pump and the solution is forced forward through the needle by the dint of the gravity and capillary force instead of pumping. The length of the needle is 25 mm but there are three sized needles in diameter (14 G, 16 G and 18 G). The needle size in gauges correlate with the diameter so that 14 G needle is equivalent to the needle with the diameter of 1.628 mm, 16 G needle to the diameter of 1.291 mm and 18 G needle to the diameter of 1.024 mm [26]. The needle size is chosen by experiment and it depends on the viscosity of spinning solution. The collector plate is placed vertically to a movable holder and placed for a distance from the syringe and the needle. Assembled electrospinning equipment is presented in in Figure 3.1(a) and there is a close-up photo of the syringe and the needle in Figure 3.1(b).

The used high voltage power supply is Chargemaster, BiPolar Electrostatic Generator, by Simco. The applied voltage is conducted via electric cord to the needle

(a) (b)

Figure 3.1: *Electrospinning apparatus. Left: A glass syringe with a needle and a copper collector plate covered by a red paper. Right: The glass syringe and the metallic needle. A positive voltage is conducted to the needle via the metallic fast coupling connected to the root of the needle.*

and the collector plate. Positive pole is connected to the root of the needle and the negative pole is connected to the collector plate via metallic fast couplings. The maximum voltage which is possible to apply is ±50 kV. Among the applied voltage, the strength of the electric field depends on a distance between the needle tip and the collector plate. The power of the electric field can be determined as a ratio of the distance to the voltage difference between the needle and the collector plate. Experimental studies have shown that the optimal strength of electric field is 2.67 kV/cm, the maximum voltage input is ±20 kV and the distance between the needle and the collector should be under 20 cm in case of the current apparatus. Parts of the electrospinning device are presented in Table 3.3.

Table 3.3: *Electrospinning device and changeable parameters of it.*

Power supply	Charge master, BiPolar Electrostatic Generator, SIMCO, Industrial static control ±50 kV
Collector	Copper plate, Variable distance, Negatively charged
Syringe	Glass syringe without a pump, Volume <5 ml
Needle sizes	14 G, 16 G, 18 G, 25 mm, Positively charged

3.2.2 Process variations of electrospinning

The spinning process consist of preparation of polymer solution, assembling the spinning equipment and finding out suitable processing parameters during the spinning process. Different needle sizes, voltage inputs and collector distances are examined to achieve constant spinning jet. The spinning process is carried out in fume chamber. In the beginning the spinning apparatus is assembled, and half of the glass syringe is filled with polymer solution. Solution is pumped through the needle so that a droplet is formed on a tip of the needle. Collector bed, a baking paper with paperboard frames, is placed on the metallic collector plate and the voltage input is turned on. Trials are done by studying different voltage inputs starting from lower voltage value and increasing it step by step. First short distance between the needle and the collector is used and the distance is kept constant while changing voltage values. After voltage studies the spinning distance is increased by one step and voltage studies are repeated. Schematic presentation of electrospinning studies is presented in Table 3.4.

Table 3.4: *Electrospinning process variations.*

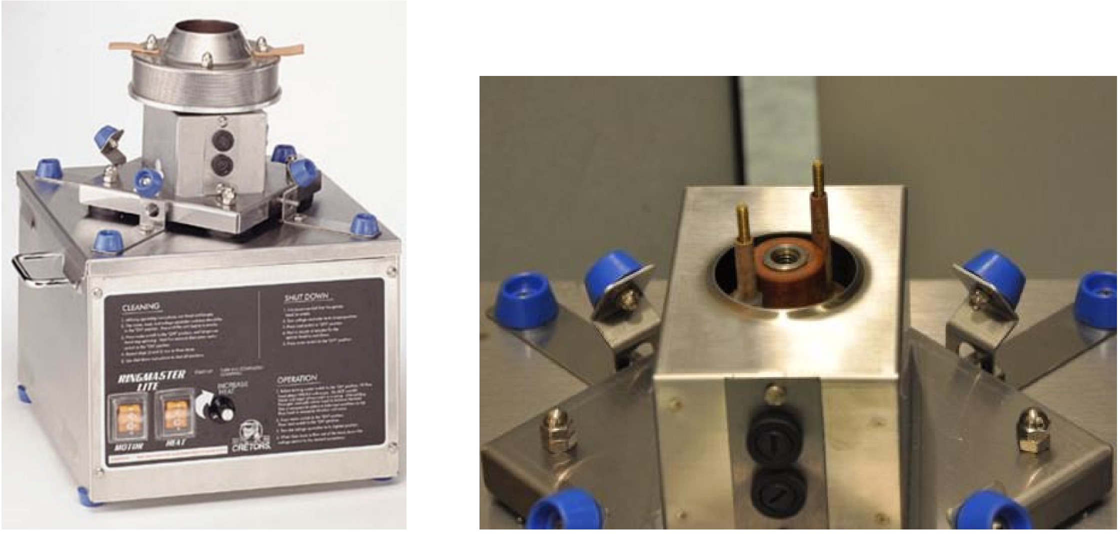
Needle size (gauges,mm)	**Distance (cm)**	**Regulated voltage (kV)**	**Electric field (kV/cm)**
16G25	10	±10 / ±15 / ±20	2.00 / 3.00 / 4.00
16G25	15	±10 / ±15 / ±20	1.33 / 2.00 / 2.67
18G25	10	±10 / ±15 / ±20	2.00 / 3.00 / 4.00
18G25	15	±10 / ±15 / ±20	1.33 / 2.00 / 2.67
Room humidity and temperature			

The quality of the spinning jet is estimated by visual observation of the jet and the fiber forming area. Only one polymer jet from the droplet is desired and the jet should be smooth and silent and it should not splash. Splashing jet and cracking noises are signs of jet instability which may lead the formation of beads and beaded fibers. Also wrong sized needle and clocking of the needle cause splashing. Usually the size of the needle can be chosen in the beginning of the process by determining whether the droplet of the solution is formed in the top of the needle or not. Too big needle let the solution pour out the needle and if the needle is too small, solvent may evaporate too quickly and clock the needle. Fibers should be uniformly distributed to the forming area. Round shape holes in the fiber mat tell on the solvent residues in fibers. Solvent residues can dissolve even already formed fibers and cause holes to the mat. However best processing parameters can not be determined until microscopy examinations of samples are done, due to a quality of formed fibers can not be seen without any magnifying tools.

3.3 Rotational melt spinning

3.3.1 Rotational melt spinning device

Initially the rotational melt spinning device is commercial device for processing of sugar and it consist of a rotor, a rotating built-up spinneret with a heating element and a detachable collector bowl around the spinneret. RMS-device is modified to be more suitable for processing of polymers but permanent changes for the engine body are not desired. RMS-device with original spinneret is shown in Figure 3.2(a) and technical details are presented in Table 3.5. A rotor and a rotating base with two metallic tenons for voltage feed, see Figure 3.2(b) are fixed parts of the machine, when the separable spinneret with the heating element is built-up on the base part. A heating element is affixed to the metallic tenons and the heating temperature is controlled by voltage regulator. The rotating part has a constant rotation speed at 2800 rpm with no slow motion scope. The spinneret starts to rotate at high speed after turning on the rotor.



(a) (b)

Figure 3.2: *Cretors Ringmaster Lite. (A) Cretors Ringmaster Lite cotton candy machine with orifice band spinneret but without a collector bowl [11]. (B) Stripped-down version of the machine, base for the spinneret with two voltage tenons.*

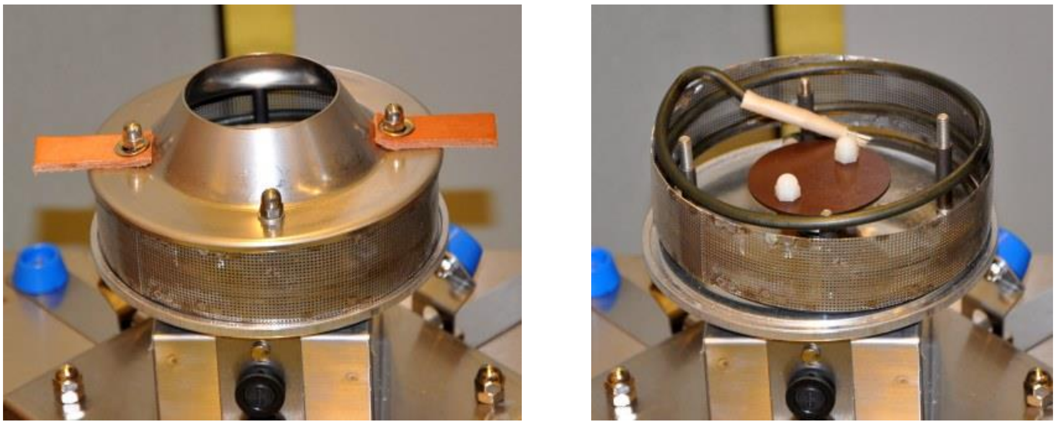
The device has two switch keys for controlling rotation and heating, a main switch and a switch for the heating. In the initial situation the main switch turns rotation on and it should be turned on before the voltage input, meaning that only rotating spinneret can be heated. The only permanent change which is done to the device is electrical modification where the heating is separated from rotation. After the modification the voltage input is able to turn on although the the main switch is not turned on, and heating of stationary spinneret is possible. The heating is voltage

Table 3.5: *Rotational melt spinning machine.*

Type	Cretors Ringmaster Lite, RMLE-X
Manufacturer	Cretors, Chicago, IL, USA
Voltage	230 V
Frequency	50 Hz
Power consumption	5 A
Rotation speed	2800 RPM

regulated and the heating level is adjusted by an additional knob with stepless control. The linear reading scale from 0 to 10 with scale division of half degree is written next to the voltage regulator knob. The device does not contain a thermoelement for adjusting the exact temperature value and the spinneret temperature is measured by infrared thermometer (Fluke 62 Mini) from the surface of the spinneret.

The original spinneret is orifice band spinneret (Obs) and it consist of a bottom plate, a top cap and a metallic orifice band which is placed between them. A circular shape tube resistor is located in a ring of the spinneret, just inside of the orifice band. The diameter of the spinneret is 14 cm and the reservoir is 3-4 cm height. The resistor tube is 5 mm in diameter and around 34 cm long and it is turned three times round the center of the spinneret. The assembled spinneret with two leather flaps on the top of the reservoir is shown in Figure 3.3(a) and the interior of the spinneret is shown in Figure 3.3(b). Openings of the orifice band are circular and they are located in grid shape. The diameter of the opening hole is 1.1 mm and the length of openings is 0.5 mm. Distance between two openings are 0.8 mm in horizontal direction and 0.9 mm in vertical direction. The dimensions of Obs is presented in Table 3.6.



(a) (b)

Figure 3.3: *Orifice band spinneret of rotational melt spinning machine. A) Assembled orifice band spinneret with two leather flaps on the top of the reservoir. B) An interior of the orifice band spinneret.*

Table 3.6: *Original orifice band spinneret.*

Diameter of the spinneret	14 cm
Orifice band	
Diameter	13.1 cm
Height	32.5 mm
Thickness	0.5 mm
Diameter of circular openings	1.1 mm
Position of openings	Grid shape Horizontal distance of 0.8 mm Vertical distance of 0.9 mm
Resistor	
Diameter of resistor tube	5 mm
Length of the resistor	34 cm

Before this study, few modifications for the orifice band spinneret are done. Tight metallic web bands are used on the outside and on both sides of the original orifice band. Additionally and extra band with small drilled notches on the bottom is placed next to the inner side of the resistor ring. Notches are 2 mm wide and approximately 0.3 mm height. The band is designed to let only completely melted polymer through. The idea is to make the polymer melt constantly before ending up to the outermost orifice band and rejecting burning of the polymer by avoiding the direct contact of polymer and a surface of the resistor. The design of the orifice band is also modified and the original band is intend to be replaced by a slotted band with diagonal cuts or horizontal cuts as openings. However, these orifice bands are not used due to the diameters of them are a little too small which affects harmfully the rotation of the spinneret.

The tube resistor do not have optimal shape and location relative to melting of polymer and high temperatures must be used for that reason. As a trial to avoid burning of polymer tube resistor heating is replaced by hot air gun heating and meaning that the orifice band spinneret is used but the tube resistor is removed and replaced by an external heat source, a hot air gun. Two different hot air guns are used and they are presented in Table 3.7. The hot air gun from Meyer has separated compressed air blast engine and thermoelement for temperature and power adjustment. Leister hot air gun has integraded blast engine and temperature adjustment.

The orifice band spinneret showed to have limitations and disadvantaged like high volume along with inefficient heating system and open reservoir. The spinneret is decide not to modify any further and due to that, there is a need for new type of spinneret. The purpose is to achieve constant melting of polymer and for that reason the cup-and-cover type spinneret, presented in 2.7, is thought. Fixed parts

Table 3.7: *Hot air guns.*

Hot air gun 1	**Hot air gun 2**
Meyer 4/00	Leister
1000 W	1600 W
230 V	7 A
1 IP 2922001	CH-6060-Sarmen
Separated compressed air blast engine	Integrated blast engine
Temperature and power adjustment via thermoelement	Integrated temperature adjustment

of the RMS-device reject the design of the cup-and-cover type spinneret. Due to voltage tenons are fixed to the rotating base, the heat source must rotate too. In addition, the only place to fix the spinneret is between two voltage tenons in the middle of the engine body. Voltage tenons are approximately five centimetres long and there are two options how they can be located in relation to the reservoir cup. The cup can be placed above the tenons making the construction unstable or the cup can be placed on lower level when voltage tenons must pierce the cup. In addition electrical connections must be able to couple taking electrical safety into account. These demands and limiting factors of design are not easily solvable and for that reason, the cup-and-cover type spinneret is not carried out.

A new spinneret which is carried out is a mould which is assembled from two plates, a bottom plate and a top plate. Two plates are fasten up together and they rotates about their axis. A polymer reservoir is a pit in the middle of the bottom plate and four furrows, which resemble spinning nozzles, leave from the reservoir pit ending up to the ring of the plate. In the middle of a cover plate is a pit to enlarge the volume of the reservoir. Due to the closed reservoir the spinneret is designed only for batch processing. The mould spinneret is heated up with two plate resistors, placed under and upper side of mould. Resistor plates with diameters of 12 cm are ordered from Oy Meyer-vastus Ab. They are stainless steel plated mica resistors with maximum surface output of 4 W/cm^2. Two insulator plates are placed both sides of the spinneret. The bottom insulator plate is fixed to the engine body of the RMS-device and mould plates are then fixed to the bottom plate.

The first assembled mould is made of polytetrafluoroethylene (PTFE) for purpose of testing new spinneret type. PTFE is not ideal spinneret material due to material softness, coefficient of heat convection and resistance for temperature deformation [13]. This means that PTFE may resist heat transfusion and it may deform under high temperatures. Despite these properties, PTFE is chosen to these very first trials due to light weight and easy machinery of the material. [13] PTFE plates are 12 cm in diameter and four tapering furrows as spinning nozzles leave from the reservoir pit and end up to small drilled holes as openings. Plates are approximately

1 cm in height and diameter of opening holes are 1 mm. Due to the PTFE mould found out to be potential for polymer processing with the existing machine, a second plate mould is fabricated from stainless steel. Stainless steel mould is overall a little smaller than the PTFE mould. The diameter of the spinneret is 11.5 cm and it is assembled from two 7 mm thick plates. A cross-section of the bottom mould plate with dimensional measurements is presented in Figure 3.4. In the middle of the plate is a polymer reservoir having a volume of approximately 4.4 ml. Four nozzles are slightly over 4 cm long and the widths of them get smaller step by step starting from 8 mm and ending up to 3 mm wide section. The narrowest part of the nozzle is followed by 0.5 mm wide spinning hole. The tapering furrow spinneret and assembling of it are shown in Figure 3.5.

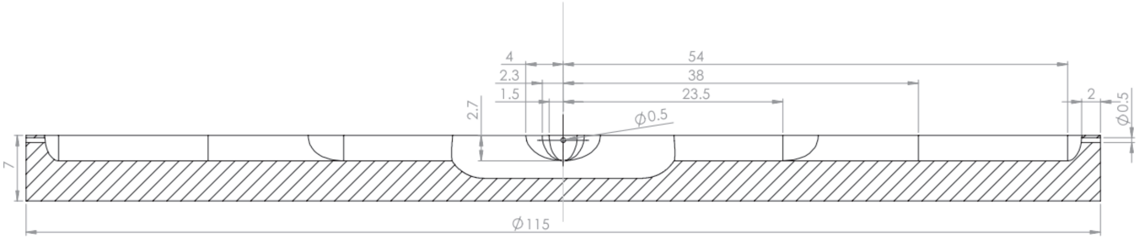
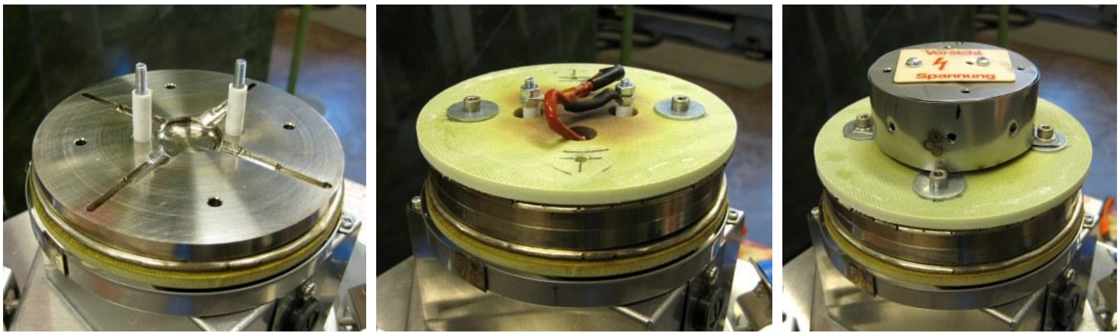


Figure 3.4: *A schematic drawing of the bottom plate of the plate mould spinneret with tapering furrows. In the middle is a polymer reservoir and transverse cross-section of furrows. Longitudinal cross-sections of nozzles are shown in both sides of the reservoir.*



(a) (b) (c)

Figure 3.5: *(a) A bottom plate is placed on the rotating base. A thin metallic band under the spinneret is an electrical safety band. (b) A cover plate, upper resistor plate and top plate are placed on the bottom and electric cables of the resistor are connected with two voltage feed tenons. (c) Assembled spinneret with top hat.*

The stainless steel mould with tapering furrows is the most used spinneret in this study but still the design is not optimal. The spinneret could be modified further by blocking up existing openings and renew them by smaller ones. Instead of downsizing openings of the existing mould plate, a new bottom plate with different design is carry out. The new spinneret mimic the cup-and-cover type spinneret having four widening furrows which end up to wide gap cavities between the bottom plate and the cover plate. The design of the bottom plate is determined by fixed parts of the machine and the dimensions of the top plate. Gap cavities are designed to be as wide as fit between two mounting holes. Nozzles are approximately 4 cm long and they widen evenly. Two nozzles are narrower starting from the width of 10.5 mm and ending up to almost 20 mm wide opening when the other two nozzles widen from 15 mm to almost 40 mm. Nozzles have three transverse sections with different depths. The final section is the opening cavity and it is 0.1 mm deep and approximately 9 mm long. A schematic cross-section drawing of the mould plate with widening furrows is presented in Figure 3.6.

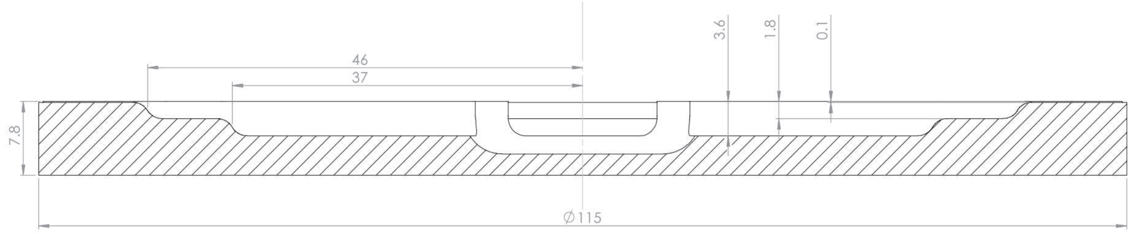


Figure 3.6: *A schematic drawing of the bottom plate of the plate mould spinneret with widening furrows. In the middle is a polymer reservoir longitudinal cross-sections of nozzles are shown in both sides of the reservoir.*

Collector bowls are used for fiber gathering. An original collector is a detachable aluminun bowl with diameter of 65 cm and height of 23 cm. The bowl is placed around the spinneret so that the bottom of the collector bowl lower 10 cm from the spinneret. A detachable plastic web is fixed on the inner wall of the bowl to prevent the polymeric floss to collapse to a bottom of the bowl. A breathable web wall collector is used to achieve more efficient cooling of fibers. The web wall collector consist of a round shape bottom plate with 8 parallel vertical sticks located in the ring of it and a separable plastic web wall which is fixed to sticks. Breathable walls let the spinneret caused air flow thorough the walls and prevent the increase of collector temperature and the formation of counter air flow. Fibers are able to flow and stretch. The diameter of the collector bowl is 70 cm and the height of the wall is 30 cm. The bottom plate of the collector is placed on hold up knobs and the bottom of the collector is 3-4 cm lower than the spinneret. In few trials web wall collector is placed on lower level resulting that the bottom of the collector is 14 cm from the spinneret. The hole in the middle of the bottom plate is enlarged and the engine body of the machine is covered by protective web collar. The purpose of the lowered collector is to prevent fiber ploughing into the bottom of the collector bowl before fibers are cooled and solidified properly.

3.3.2 Process variations of rotational melt spinning

Different processing variations including materials, design of the device, heating and cooling combinations are presented in this subsection. Processing variations are categorized according to different spinnerets and according to polymers processed via the spinneret. Similar rules are followed in sample naming system. An example is given in Equation (3.1) where the last number corresponds to the sample number.

$$\underbrace{\text{RMS}}_{method}\_\underbrace{\text{Obs}}_{mould}\_\underbrace{\text{PLDLA96/4}}_{polymer}\_1 \tag{3.1}$$

The abbreviations are then presented in Table 3.8. The rotation parameters as well as the heating parameters are shown in parenthesis. The rotation time corresponds to the time from the beginning of the preheating to the time when the actual rotation starts. The temperature is then the preheating temperature of the polymer. The only heating parameter refers to the heating intensity. It should be noted that all experiments are done in room temperature.

Table 3.8: *Abbreviations used in the sample naming and description of processing parameters in tables.*

Abbreviation	Definition
RMS	Rotational Melt Spinning
Obs	Orifice band spinneret
TmTf	PTFE mould with Tapering furrows
SmTf	Steel mould with Tapering furrows
SmWf	Steel mould with Widening furrows
R	Rotation parameters (time , temperature)
H	Heating parameters (heating level)

Process variations with orifice band spinneret

Orifice band spinneret (Obs) and P(L/D)LA 96/4 are used in preceding trials. The construction of Obs was changed by adding two tight extra web bands on both sides of the original orifice band and spinning trials were repeated after removing the outermost web. Also the original orifice band and the tight web band were used on their own. Obs with open material reservoir enables both batch processing and continuous polymer feeding. Continuous feeding at constant feed rate has been tried in earlier studies but it has resulted to uneven melting and clogging of the openings. Thus batch processing is chosen to this study. Polymer adding into cool reservoir but also into preheated reservoir were studied with no remarkable differences. Processing parameters of preceding trials are presented in Table 3.9 and the naming system is little different than in later trials.

Table 3.9: *Preceding trials which are done with orifice band spinneret. In case of three webs, two tight webs are placed both sides of the original orifice band.*

Processing	Spinneret	Processing variations
RMS_1	Obs with three webs	R+H (15 o'clock) Polymer adding after heating of the spinneret
RMS_2	Obs with three webs	R+H (14 o'clock) Polymer adding after heating of the spinneret
RMS_3	Obs with three webs	R+H (16 o'clock) Polymer adding after heating of the spinneret
RMS_4	Obs with three webs	R+H (18 o'clock) Polymer adding after heating of the spinneret
RMS_5	Obs with three webs	Polymer adding into cool reservoir R+H
RMS_6	Obs with three webs	Polymer adding into cool reservoir R+H
RMS_7	Two webs, the outermost tight web is removed	Polymer adding into cool reservoir R+H
RMS_8	Original orifice band	Polymer adding into cool reservoir R+H
RMS_9	One tight web band	Polymer adding into cool reservoir R+H
RMS_10	Orifice band and extra band with notches	Polymer adding into cool reservoir R+H

In this study processing temperatures are tried to optimize but the geometry is not modified further. Extra band with small drilled notches is used inside the orifice band spinneret. Approximately 10 g of P(L/D)LA 96/4 granules are used in time and the material is placed in the middle of the spinneret reservoir in the beginning of the spinning process. First the motor is turned on and the heating is turned on in few seconds. Suitable heating ranges are studied. An efficient heating at maximum level but also a careful heating up to the predetermined temperature value has studied. Aluminium collector bowl is used and fibers are collected by long tweezers during processings. Processing times vary between 11-14 minutes in each processing. Parameters are presented in Table 3.10.

Table 3.10: *Parameters for rotational melt spinning of P(L/D)LA 96/4 by orifice band spinneret with extra band. Rotation and heating are both turned on in the beginning of the processing.*

Processing	**Rotation + Heating (heating level)**	**Collector type and notes**
RMS_Obs_PLDLA96/4_1	R + H(10)	Aluminium bowl
RMS_Obs_PLDLA96/4_2	R + H(7,7.5,8)	Aluminium bowl
RMS_Obs_PLDLA96/4_3	R + H(8)	Aluminium bowl

In case of hot air gun heating, polymer granules of P(L/D)LA 96/4 are placed inside the spinneret and rotation is turned on. Polymer is heated by hot air gun which is placed on the open reservoir. Hot air flow and centrifugal forces push the polymer forward. Approximately 5 g of P(L/D)LA 96/4 is used in time and it is heated first by hot air gun 1 and then by hot air gun 2. The temperature is adjusted up to 220 °C via hot air gun 1 and even up to 600 °C via hot air gun 2. Temperatures of the spinneret are much lower, in range of 130 − 160 °C, measuring by infrared thermometer. Processing time is tens of minutes.

Process variations with tapering furrow plate mould spinnerets

Plate mould spinnerets are used for processing of several polymers. The spinneret type is designed only for batch processes and the reservoir is filled up with polymer granules while assembling the the spinneret. Approximately 5 g of polymer is able to use in time and different processing set ups are studied. Temperatures are measured from the surface of the spinneret plates by infrared thermometer.

The PTFE mould with tapering furrows is used to evaluate the potentiality of plate mould spinnerets and it is used only once for processing of P(L/D)LA 96/4. Rotation is turned on before careful heating from level 5 up to level 10. The motor is turned off couple of times during the processing and small nozzle holes are drilled open once. The temperature increased up to 170 − 180 °C during the processing and the entire processing time was over 20 minutes. The aluminum collector bowl is used and fibers are collected by long tweezers. Processing parameters are presented in Table 3.11.

The stainless steel mould with tapering furrows is the most used spinneret in this study. P(L/D)LA 96/4, PDLA 50/50, PCL and PLCL 70/30 are processed with it and different heating and cooling combinations are studied. In case of each polymer the processing pattern is quite similar. First processings are done by turning rotation and heating on at the same time in the beginning of the process. The

Table 3.11: *Parameters for rotational melt spinning of PLDLA 96/4 by teflon mould with tapering furrows.*

Processing	Rotation + Heating (heating level)	Collector type and notes
RMS_TmTf_PLDLA96/4	R + H(5,6,7,8,9,10)	Aluminum bowl

temperature regulator is turned lower after polymer comes out from the spinneret. These processes gives information about melting range of the polymer and helps to evaluate the temperature at which polymer melt viscosity is low enough for fiber forming. Preheating temperature of further trials is determined based on the fiber forming temperature. In later studies, the spinneret is heated up to the preheating temperature before turning on the rotation. Both aluminum collector bowl and web wall collector are used for each polymers.

P(L/D)LA 96/4 is processed via stainless steel mould with different heating variations presented in Table 3.12. Four first processings are done by turning both rotation and heating on in the beginning of the process. Careful heating of polymer is studied by adding the level of voltage input step by step in first processing. In later processes more efficient heating is used and the spinneret is heated at maximum level from the beginning of the process. After fourth processing, electrical changes are done to the device which enables preheating of stationary spinneret. Even as electrical alterations are done, electrical safety of the device is improved by small structural changes. Thin metallic band is placed under the spinneret and small hat is placed on the spinneret to cover electrical cables and electrical connections. After fifth processing the diameter of the top insulator plate is got little smaller to prevent the entanglement of fibers to the spinneret. When the spinneret is preheated, the temperature is let to rise up to at least 120 °C before turning on the rotation. In most of trials the motor is turned on right after the preheating temperature is reached but once the temperature is rose up to 120 °C and then tried to keep there couple of minutes before turning on the rotation. In first processings, in which rotation is turned on simultaneously with heating, fibers are collected using only the aluminum bowl. Web wall collector is used in later processings where polymer reservoir is preheated. Fibers are collected by tweezers during each processing times.

Table 3.12: *Parameters for rotational melt spinning of PLDLA 96/4 by stainless steel mould with tapering furrows.*

Processing	**Rotation + Heating R (time, temperature), H (heating level)**	**Collector type and notes**
RMS_SmTf_PLDLA96/4_1	R + H(6,8,10)	Aluminum bowl
RMS_SmTf_PLDLA96/4_2	R + H(10,8,9)	Aluminum bowl
RMS_SmTf_PLDLA96/4_3	R + H(10,9)	Aluminum bowl
RMS_SmTf_PLDLA96/4_4	R + H(10,9)	Aluminum bowl
RMS_SmTf_PLDLA96/4_5	H(10,9) + R(6:00, 120°C)	Aluminum bowl First processing after electrical changes
RMS_SmTf_PLDLA96/4_6	H(10,9) + R(11:45, 140°C)	Aluminum bowl
RMS_SmTf_PLDLA96/4_7	H(10,8) + R(9:00, 150°C)	Web wall collector leather ledges on the top of the spinneret
RMS_SmTf_PLDLA96/4_8	H(10,9) + R(10:00, 120-140°C)	Web wall collector Bottom plate has lower temperature than upper plate

Other polymers, like PDLA 50/50 with lower iv-value, are processed with stainless steel mould spinneret with tapering furrows to evaluate the usability of the spinneret. Processing variations of PDLA 50/50 is presented in Table 3.13. In first processing rotation and heating are turned on at the same time in the beginning of the process and preheating temperature for following studies is determined to be approximately 120 °C. In preheating trials reservoir is heated up and temperature is kept for a moment in predetermined temperature before turning on rotation. Aluminum collector bowl is used in first studies and fibers are collected by tweezers. In last trial web wall collector is used and fibers are collected all at once in the end of process. Electrical safety band is used under the spinneret in each time.

Table 3.13: *Parameters for rotational melt spinning of PDLA 50/50 by stainless steel mould with tapering furrows.*

Processing	**Rotation + Heating R (time, temperature), H (heating level)**	**Collector type and notes**
RMS_SmTf_PDLA50/50_1	R + H(10,9,8)	Aluminum bowl
RMS_SmTf_PDLA50/50_2	H(10,9) + R(8:35, 124°C) + H(8)	Aluminum bowl
RMS_SmTf_PDLA50/50_3	H(10) + R(9:30, 125-170°C) + H(8)	Web wall collector Fibers collected at once in the end of processing

PCL is processed by stainless steel mould with tapering furrows couple of times and processing variations are presented in Table 3.14. In first processing rotation and heating are turned on in the beginning of the process and heating is turned lower step by step. Aluminum collector bowl is used and fibers are collected in the end of the processing after the temperature of the collector bowl is cooled down. Second processing is done by preheating the spinneret up to approximately 70 °C before turning the heating down to level 9 and turning on the rotation. Web wall collector is used. All trials are done after electrical safety modifications but the metallic extra band under the spinneret is removed before the second processing.

Table 3.14: *Parameters for rotational melt spinning of PCL by stainless steel mould with tapering furrows.*

Processing	**Rotation + Heating R (time, temperature), H (heating level)**	**Collector type and notes**
RMS_SmTf_PCL_1	R + H(10,9,8,7)	Aluminum bowl
RMS_SmTf_PCL_2	H(10,9) + R(6:00, 90°C) + H(8,7)	Web wall collector Low metallic band under the spinneret is removed before the processing

Processing parameters of PLCL 70/30 spinning with stainless steel mould with tapering furrows are presented in Table 3.15. First trial is done by turning the rotation and heating on at maximum level in the beginning of the process, and turning the heating down after fibrous material starts to form. Aluminum collector bowl is used and fibers are collected all at once after the processing. Next trials are done by preheating the spinneret up to temperature range of $130 - 145\,^{\circ}\mathrm{C}$ before turning on the rotation. Web wall collector is used and fibers are collected all at once in the end of the process. The bottom resistor plate is damaged causing temperature variation between mould plates, and in last three processings the temperature of the bottom plate is clearly lower than the temperature of the top plate. Metallic safety band is removed before processing of PLCL 70/30.

Table 3.15: *Parameters for rotational melt spinning of PLCL 70/30 by stainless steel mould with tapering furrows.*

Processing	**Rotation + Heating R (time, temperature), H (heating level)**	**Collector type and notes**
RMS_SmTf_PLCL_70/30_1	R + H(10,9)	Aluminum bowl Processed before the electrical safety modifications
RMS_SmTf_PLCL_70/30_2	H(10) + R(11:00, 130°C) + H(8)	Web wall collector
RMS_SmTf_PLCL_70/30_3	H(10) + R(10:30, 120-160°C) + H(8)	Web wall collector
RMS_SmTf_PLCL_70/30_4	H(10) + R(11:00, 143°C) + H(8)	Web wall collector

Process variations with widening furrow plate mould spinneret

The bottom plate of the plate mould spinneret is replaced by a new plate with widening furrows and gap openings. Also broken bottom resistor plate is replaced by new one. Processing pattern is similar to the processing pattern with the tapering furrow spinneret which means that in first processings heating and rotation are turned on simultaneously in the beginning of the process and in later processings polymer is preheated before turning on the motor.

PLCL 70/30 result maybe most promising end products when processing with tapering furrow plate mould spinneret, and for that reason it is chosen to be the first polymer for testing of the new spinneret. Processing parameters are presented in Table 3.16. In first processing time, preheating temperature is determined to be in range of $100 - 130\,^{\circ}\mathrm{C}$. Later processings are done by preheating the spinneret before start-up of rotation. Web wall collector is used in each processing time and fibers

Table 3.16: *Parameters for rotational melt spinning of PLCL 70/30 by stainless steel mould with widening furrows.*

Processing	**Rotation + Heating R (time, temperature), H (heating level)**	**Collector type and notes**
RMS_SmWf_PLCL_70/30_1	R + H(10,8,7)	Aluminum bowl Processed before the electrical safety modifications
RMS_SmWf_PLCL_70/30_2	H(10) + R(9:00, 100-130°C)	Web wall collector
RMS_SmWf_PLCL_70/30_3	H(10) + R(9:00, 100-130°C) + H(8)	Lowered web wall collector

are collected all at once in the end of processing. In last processing, the bottom of the web wall collector is set down in lowered level so that fibers would have more space to elongate and they would not plough into the bottom of the collector bowl too early.

P(L/D)LA 96/4 is processed two times with the widen furrow spinneret. Processing parameters are presented in Table 3.17. In first processing rotation and heating are turned on at the same time, web wall collector is used and fibers are collected by tweezers. In a second processing time the spinneret is heated up to $120 - 130\,^{\circ}\mathrm{C}$ before turning the motor on. Two about 0.5 cm long and 1,5 cm wide aluminum ledges are placed under the bottom spinneret plate to change the flow field surrounding the spinneret and to prevent entanglement of fibers with the spinneret. Lowered web wall collector is used and fibers are collected by tweezers during the processing.

PDLA 50/50 is processed couple times and processing variations are presented in Table 3.18. In first processing rotation and heating are turned on at the same time and in the second time the spinneret is preheated up to $125\,^{\circ}\mathrm{C}$. Aluminum ledges which are directed downward and are placed on the bottom of the spinneret are used both times. Lowered web wall collector is used and fibers are collected all at once in the end of processing.

PCL is processed with widening furrow spinneret and processing parameters are presented in presented in the Table 3.19. Aluminum ledges are fixed under the spinneret before the processings. Preheating temperature in later processing is $75\,^{\circ}\mathrm{C}$. Lowered web wall collector is used in both times and fibers are collected in the end of the processing.

Table 3.17: *Parameters for rotational melt spinning of PLDLA 96/4 by stainless steel mould with widening furrows.*

Processing	**Rotation + Heating R (time, temperature), H (heating level)**	**Collector type and notes**
RMS_SmWf_PLDLA_96/4_1	R + H(10,8,7)	Web wall collector Fibers collected by tweezers
RMS_SmWf_PLDLA_96/4_2	H(10) + R(7:00, 120-130°C) + H(8)	Lowered web wall collector Two aluminum ledges under the spinneret

Table 3.18: *Parameters for rotational melt spinning of PDLA 50/50 by stainless steel mould with widening furrows.*

Processing	**Rotation + Heating R (time, temperature), H (heating level)**	**Collector type and notes**
RMS_SmWf_PDLA_50/50_1	R + H(10,8)	Lowered web wall Aluminum ledges under the spinneret Fibers collected at once
RMS_SmWf_PDLA_50/50_2	H(10) + R(6:30, 125°C) + H(8)	Lowered web wall collector Aluminum ledges under the spinneret Fibers collected at once

Table 3.19: *Parameters rotational melt spinning of PCL by stainless steel mould with widening furrows.*

Processing	**Rotation + Heating R (time, temperature), H (heating level)**	**Collector type and notes**
RMS_SmWf_PCL_1	R + H(10)	Lowered web wall Aluminum ledges under the spinneret Fibers collected at once
RMS_SmWf_PCL_2	H(10) + R(5:00, 75°C) + H(8)	Lowered web wall collector Aluminum ledges under the spinneret Fibers collected at once

3.4 Fiber evaluation methods

Succeeding of fiber spinning can be evaluated by determining the quality of fibers. Fiber finesses and different faults and unevenness of end-products are studied. Optical microscopy is used for initial evaluation of structures and finesses of formed fibers. Thin layer of rotational melt spun fibers are placed on petridish and covered by thin glassy plate. Black coloured paper is placed under the petridish before microscoping. Stereomicroscopy Zeiss SV 8, Germany, with magnification of up to 6.4 is used for this first step evaluation and determination necessity of further studies. Photographs are taken by a camera joined to the microscopy and fiber diameters are analysed from photos. Computer software View 2 is used for determination of fiber diameters. Round shape, bright fibers reflect and refract light making the fiber diameter determination difficult. Also the light microscopy is not suitable evaluation of fiber surface morphology. Due to an inadequate resolution, optical microscopy is used only for rotational melt spun samples.

Fiber surface morphology from selected rotational melt spun fiber samples are analysed using scanning electron microscopy, SEM. Also electrospun fibrous samples are analysed using SEM. A scanning electron microscopy has higher resolution than optical microscopy, and 35-fold magnification is the smallest and 1000-fold magnification is the highest magnification level. Thin layer of fibers are glued on the surface of brass button which is followed by gold sputtering of the sample. Samples are sputtered four times in 30 seconds periods. SEM imagining is based on scanning the surface of the sample by focused beam of electrons.

For future analysing of differential scanning calorimetry, inherent viscosity measurements, in vitro -hydrolysis tests and gel permeability testing are thought. Differential scanning calorimetry, DSC, could be used for analysing effects of fiber forming processes to polymeric material. DSC could be used to analyse the inner structure of fibers like crystallinity, weather crystals are formed and degree of crystallinity. DSC measurements can also be used for evaluation of thermal degradation of polymers during rotational melt spinning and for evaluation of polymer chain scission in the solution during electrospinning process. Inherent viscosity (iv) measurement for formed fibers could also give information about the degradation of polymers during fiber forming process. Inherent viscosity measurements are done to raw polymers for determining molecular weight and melting range, and changes of iv-values before and after fiber forming would reflect changes in molecular weights. Fiber degradation rate and change of volume caused by a hydrolytic degradation could be evaluated via in vitro -tests. Among the in vitro -testing, gel permeability test would be valuable when thinking about the usability of the formed material as a scaffold material. The gel permeability tests reflects wetting properties of the material.

4. RESULTS AND DISCUSSION

4.1 Results of electrospinning

Optimal solution properties and spinning parameters are determined by experiment. Quality of spinning jet is observed during the spinning process and best processing parameters are evaluated. Smooth and silent spinning jet with no sparkling is an objective. Sample is manufactured after the spinning jet is stabilized and fiber formation seems to become constant. End-products are then studied by SEM by estimating the presence and the amount of different fiber faults. Fiber diameters are measured from 30 randomly selected fibers and average diameters and standard deviations are calculated. Best processing parameters for each solution are presented in Table 4.1 and fiber diameters are presented in Table 4.2.

Table 4.1: *Best processing parameters for each electrospinning solution.*

Sample	Needle size (gauges,mm)	Distance (cm)	Regulated voltage (kV)	Spinning time (h:min)	Grammage of end-product (g/m^2)
ES_PLDLA_70/30_1	18G25	10	±15	3	59.8
ES_PLDLA_70/30_2	18G25	15	±15	1	3.6
ES_PLGA_80/20	18G25	15	±10	1:15	1.9

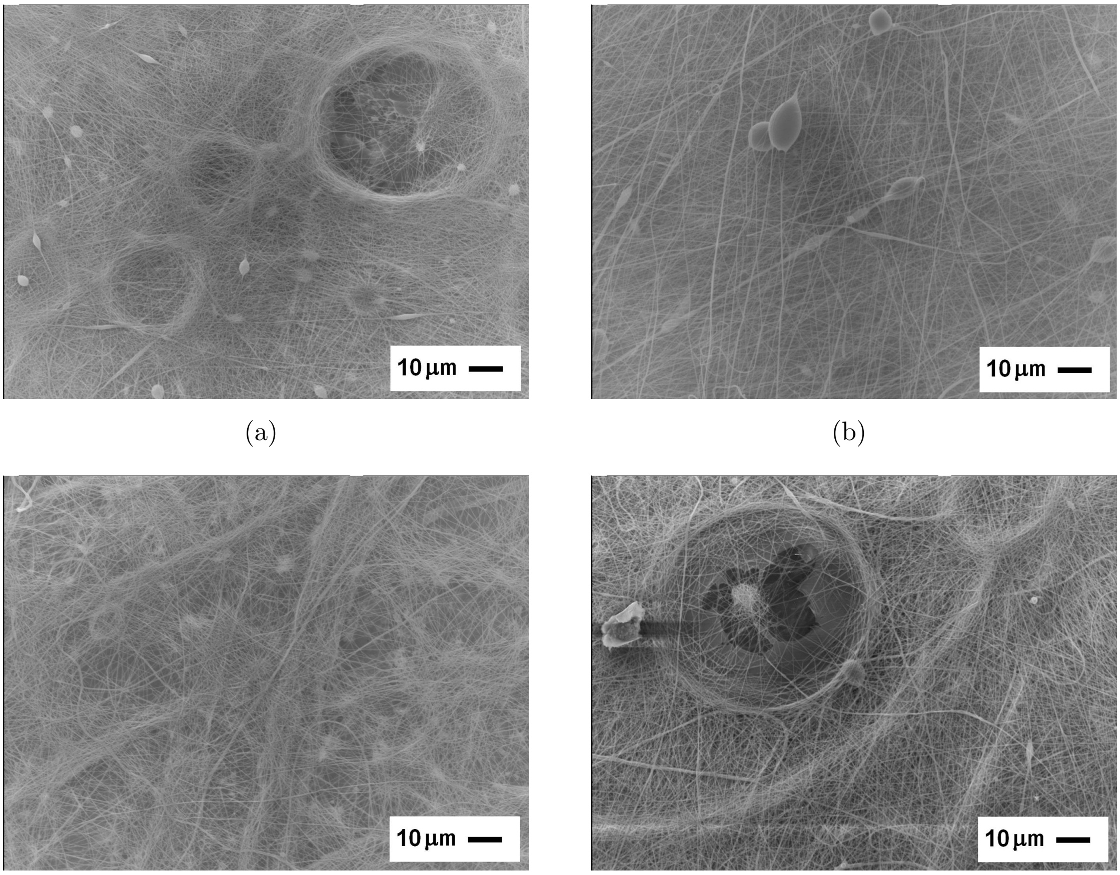
Table 4.2: *Results of electrospinning of three different polymer solutions. Fiber diameters are measured from 30 randomly selected fibers and the average value and standard deviations are calculated. Dimensions are given in μm.*

Sample	Fiber diameter range (μm)	Average fiber		Average bead	
		diameter	std	diameter	std
ES_PLDLA_70/30_1	0.21-0.84	0.36	0.17	3.74	2.55
ES_PLDLA_70/30_2	0.11-0.29	0.19	0.04	-	-
ES_PLGA_80/20	0.19-0.86	0.44	0.20	-	-

4.1.1 Results of electrospinning of poly-L,DL-lactide 70/30

First electrospun PLDLA 70/30 solution, with mass percent of 8 %, is two weeks old at the processing time. The viscosity of the solution seems to be decreased from the initial value and smaller capillary needle, in size of 18 G, is used. Voltages of ±15 kV are used with spinning distance of 10 cm. Fibers are settled in parallel order in different layers in the sample. Fibers are mostly round shape and diameters vary between 0.21-0.84 μm. Fiber fractures exist and beads are formed despite of changing the needle size. The average bead diameter is 3.74 μm. Fibers and beads are shown in Figures 4.1(a) and 4.1(b). After two weeks from the spinning process, the same solution and same spinning parameters are used. Number of beads are multiplied. Bead formation is most probably caused by polymer degradation in too old spinning solution. Round shape pits are found from the sample, which are result of solution droplets. The residual solvent is dissolved already formed fibers on the collector plate.

Solution properties like viscosity changed during the ageing of the solution and new solution is prepared with 9 m-% of polymer. Some impurities are dissolved into the solution from the lid of the storing bottle, which later caused colouring of the solution and decrease of the viscosity. Spinning parameters are similar to the first solution but the distance between the needle tip and the collector is now 15 cm. Fiber forming is slow and fibers settled unevenly on the collector, which is shown in Figure 4.1(c). Fiber diameter distribution is smaller than in the previous sample and diameters vary from 0.11 μm to 0.29 μm. Round shape pits, like in Figure 4.1(d), are formed when solution droplets are ended up to the collector surface.



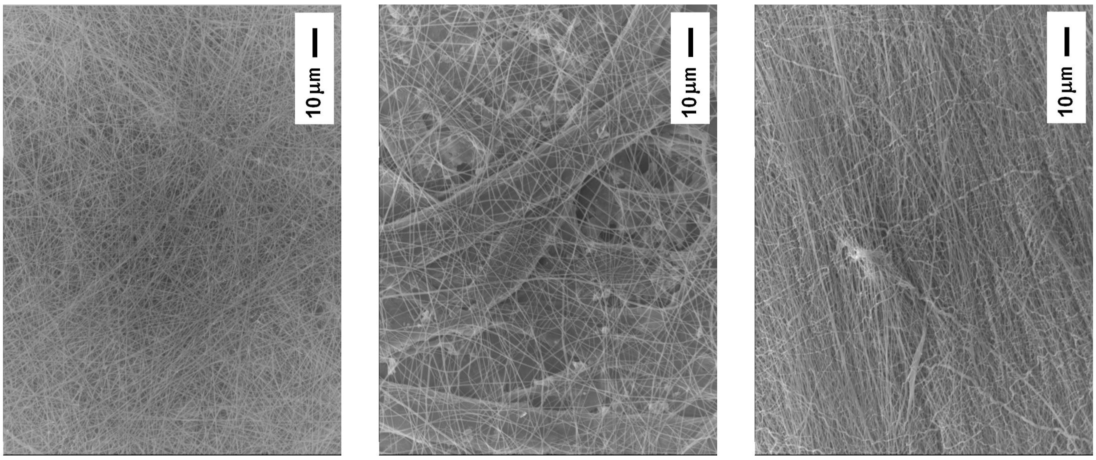
(a) (b)

(c) (d)

Figure 4.1: *End products of electrospinning of PLDLA 70/30. Polymer, polymer concentration, needle size, collector distance, voltage difference are reported. (a) PLDLA 70/30: 8 m-%, 18G25, 10 cm, 30 kV. Solution droplets are ended up to the collector. (b) PLDLA 70/30: 8 m-%, 18G25, 10 cm, 30 kV. Fibers and beads. (c) PLDLA 70/30: 9 m-%, 18G25, 15 cm, 30 kV. Fibers are settled unevenly on the collector plate. (d) PLDLA 70/30: 9 m-%, 18G25, 15 cm, 30 kV. Solution droplets are ended up to the collector surface.*

4.1.2 Results of electrospinning of poly(L-lactide-co-glycolic acid) 80/20

A solution from PLGA 80/20 with mass percent of 12 % is spun using 18 G needle and 15 cm distance between collector and the needle tip. The voltage input is ±10 kV. Fibers are smooth and beads are not formed, see Figure 4.2(a). Fiber diameters vary between 0.19-0.86 μm and casual differences in diameters are shown in few fibers. Fiber breaks exist evenly in the sample and few thick and curled fibers are found. New solution batch with polymer concentration of 13 m-% is spun using same spinning parameters with the exception of voltage difference of 30 kV. End product is mostly similar to the previous sample but some rough parts and thick fibers are found like in Figure 4.2(b). Fiber breaks exist and the sample contain regions where fibers are curled, like in Figure 4.2(c).



(a) (b) (c)

Figure 4.2: *End products of electrospinning of PLGA 80/20. Polymer, polymer concentration, needle size, collector distance, voltage difference are reported. (a) PLGA 80/20: 12 m-%, 18G25, 15 cm, 20 kV. Smooth fibers from 12 m-% solution. (b) PLGA 80/20: 13 m-%, 18G25, 15 cm, 30 kV. Smooth fibers on the top, thick fibers and roughness on the bottom. (c) PLGA 80/20: 13 m-%, 18G25, 15 cm, 30 kV. Curled fibers which can be found from both samples.*

In general, there is no remarkable differences between electrospinning of PLDLA 70/30 and PLGA 80/20. Both polymers are spinnable, unlike P(L/D)LA 50/50. The study of P(L/D)LA 50/50 is discontinued due to poor success. The biggest difference between electrospinning of PLDLA 70/30 and PLGA 80/20 is shown in solution concentrations. PLDLA 70/30 is spinnable with lower solution concentrations than PLGA 80/20. Concentration of 8 m-% is suitable for PLDLA 70/30 when PLGA 80/20 requires polymer concentration of 12 m-%. PLDLA 70/30 fibers are quite even with fiber diameters between 200-300 nm when PLGA 80/20 result to fiber diameters of 200-400 nm. Beads are not formed in spinning of PLGA 80/20, when PLDLA 70/30 samples contained beads. Polymer concentration seems to have influence in fiber breakages and bead formation, which both become more frequent with decreasing polymer concentration and viscosity of the solution. Processing parameters, like induced voltages, needle size and the collector distance from the needle, show to have influence in sparkling of the solution and formation of solvent consisting beads. Nevertheless, processing parameters do not affect fiber morphology.

4.2 Results of rotational melt spinning

In this result observation, quality of end products and succeeding of processing are studied. To evaluate the quality of end products, visual evaluation by optical microscopy is done to all samples. Fiber diameters and faults are estimated on the strength of the visual observation. Fiber diameters are measured from 15-30 randomly selected fibers. Fiber surface structures are studied by scanning electron microscopy from a few selected samples. The easiness of parameter controlling and effect of processing parameters to end-products are estimated for overall evaluation of the process. The main result of the work is to evaluate the applicability of the method and usability of the spinning device.

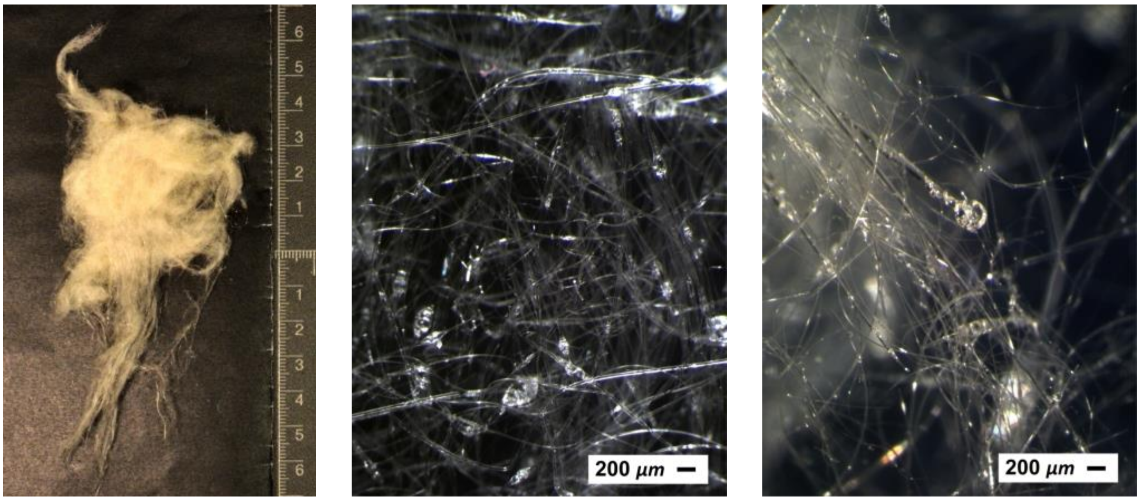
4.2.1 Results with orifice band spinneret

Preceding trials with P(L/D)LA 96/4 have been resulted to rough fibrous material with quite short fiber lengths. Fiber diameter distribution has been wide, varying commonly between 15-65 μm. The ratio of thin and thick fibers has differed depending on the sample but all samples contained relatively huge amount of thick fibers. Fibrous material contained beads and needles with diameters up to over 300 μm. Processing notes and results are collected into the Table 4.3. Fiber diameters are tried to decrease by restricting the amount of out-coming polymer with different orifice bands and by reducing the size of orifices. There is not much information about processing available but the method is evaluated to be potential for fiber forming.

Also in this study spinning of PLDLA 96/4 with the orifice band spinneret results to rough and burned fibrous material. In Table 4.4 is presented summary of spinning results and in Figure 4.3(a) is shown an overal look of the sample. Fiber diameter distribution is wide, from 8 to 40 μm, and fibrous material contain faults like swelled parts, see Figures 4.3(b) and 4.3(c), and beads in range of 130-200 μm. Some beads are found in the end of fibers but also loose beads are mixed to the fibers. Swelled parts contain air bubbles which are a signal of too high temperature combined with too low pressure. Length of the fibers are short, in range of few centimeters, but exact values are not known due to fibers are partly melt together and separation of one fiber from the floss do not succeed. Beads and needles are formed in the beginning of the process and relatively much polymer is wasted due to the bead formation. The very first fibers are thicker than fibers which are formed in the end of the process. This means that in the beginning of the process fibers do not stretch as much as in the end of the process which shows that polymer melt is too viscous for fiber forming in the beginning. Efficient heating at top heating level in the beginning of the process showed to be the best alternative. Rapid melting and rapid increase of the melt temperature are desired. High processing temperatures are required due to rotation cools down the spinneret and the open reservoir causes heat loss, but also due to the short contact time between polymer and resistor surface. As disadvantage polymer burns easily.

Table 4.3: *Results of preceding trials which are done with orifice band spinneret. Processing temperatures are measured from the surface of the resistor (T_{res}) and from the middle of the spinneret (T_{mid}).*

Processing	**Results and notes**
RMS_1	T_{res}=180°C, T_{mid}=220°C Too big fiber diameters 12-64 μm
RMS_2	T_{res}=130°C, T_{mid}=160°C Thicker fibers than in previous trial 20-86 μm
RMS_3	T_{res}=185°C, T_{mid}=250°C Thinner fibers than before, but still too thick fibers 15-65 μm
RMS_4	T_{res} >270°C, T_{mid}=195°C 15-54 μm
RMS_5	T_{res}=120°C, T_{mid}=250°C Large amount of needles 13-30 μm
RMS_6-10	Samples 6-10 are very similar to previous samples Very thick needles



(a) (b) (c)

Figure 4.3: *(a) A photo of fibrous PLDLA 96/4, sample RMS_Obs_PLDLA_96/4_2. A measuring line segments are in centimetres. (b-c) Sample RMS_Obs_PLDLA_96/4_2, mag 3.2x, swelled parts*

Table 4.4: *Evaluation of RMS process and visual examination of PLDLA 96/4 fibers spun by orifice band spinneret.*

Processing	**Fiber diameters,** **Sample evaluation**	**Processing time and notes**
RMS_Obs_PLDLA_96/4_1	Burned, yellowish-brown fibers, Full of brown beads	Processing interrupted Too high temperature
RMS_Obs_PLDLA_96/4_2	8-40 μm, beads 40-114 μm Little burned Beads in the middle of fibers Air bubbles in swelled parts	13:30 Beads and needles formed in the beginning Polymer is too long time in too high temperature
RMS_Obs_PLDLA_96/4_3	7-40 μm, beads 130-190 μm Yellowish fibers Fibers partly melted together Beads and air bubbles in the middle and in the end of fibers	11:30 Beads and needles formed in the beginning Smell of burning Uneven sound in processing

As an objective to avoid burning of polymer, hot air gun heating is studied but results are not promising. The method resembles melt blowing but the heating temperature is too low for fiber forming process despite that rotation is occasionally turned off during the processing. All material do not melt and unmelted granules are found inside the spinneret. However most of the material melt but the viscosity of the material is too high for formation of fibers. Melted material get stuck inside the spinneret. However Only thick needles or rods are formed with diameter of millimeters instead of micrometers. Formed material is so rough that visual observation is done without any magnifying tools.

As a conclusion of spinning processes with orifice band spinneret, the design of the spinneret with open and large reservoir is not ideal for processing of polymers. Heat loss from the spinneret is too high for efficient melting of polymer. At the same time, burning of polymer cause problems when tube resistor heating is used. In all cases temperature controlling is difficult. Also the design of orifices is not optimal for processing of viscoelastic polymers due to high ratio of the opening diameter to its length. Polymer chains may not have time to orientate and they resist stretching of fibers. For these reasons the spinneret is decided not to modify any furhter.

4.2.2 Results with plate mould spinneret with tapering furrows

The plate mould spinneret with tapering furrows has two variations, a PTFE mould and stainless steel mould. PTFE mould is used once with P(L/D)LA 96/4 for evaluating the potentiality of the new spinneret type and results are presented in Table 4.5. Due to rotation and heating are turned on in the beginning of the process and spinneret is heated carefully, the processing time is quite long, over 20 minutes. Partly due to long processing time, deformation of the PTFE mould occurrs. PTFE plates expand and the crack between two plated enlarge little. Rotating motion cools down the ring of the mould which causes clogging of orifices when temperature of polymer decreases and viscosity increases. Fibers are more uniform quality than fibers processed with orifice band spinneret, see Figure 4.4. PTFE mould result to fibrous material with fiber diameters varying between 9-40 μm. Different sized fibers are evenly distributed resulting to material with soft feeling. Due to plate deformation, small amount of polymer is able to come out from the crack between mould plates and flat ribbon type material is formed instead of round shape fibers. Fibrous material do not contain swelled parts like in case of orifice band spinneret.

Table 4.5: *Optical evaluation of rotational melt spun PLDLA 96/4 fibers fabricated by PTFE mould spinneret with tapering furrows.*

Processing	Fiber diameters, Sample evaluation	Processing time and notes
RMS_TmTf_PLDLA96/4	9-40 μm Fibers partly melt together Evenly distributed different sized fibers Soft feeling Film like ribbon	14:30+8:50

Part of the fibers are melt together when hot fibers plough into each other. It can reflect poor design of the device, like too large openings of orifices or too small distance between two openings. The new spinneret type seems to be promising and more suitable for processing of polymer compared to orifice band spinneret. More homogenous fibrous material is possible to produce but still fibers are not able to stretch enough. Other disadvantage is that the temperature decrease in the ring of the rotating spinneret and temperature cools down in most critical part of the spinneret.

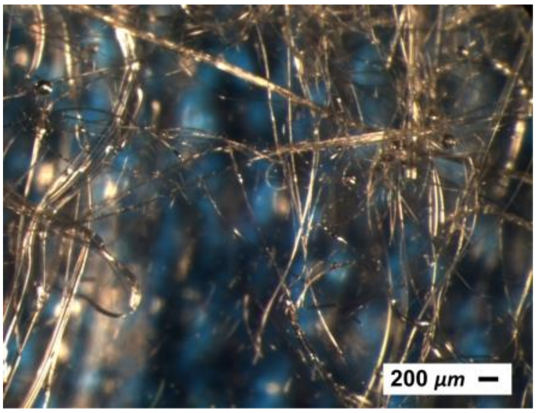


Figure 4.4: *PLDLA 96/4 fibers manufactured with PTFE plate mould spinneret.*

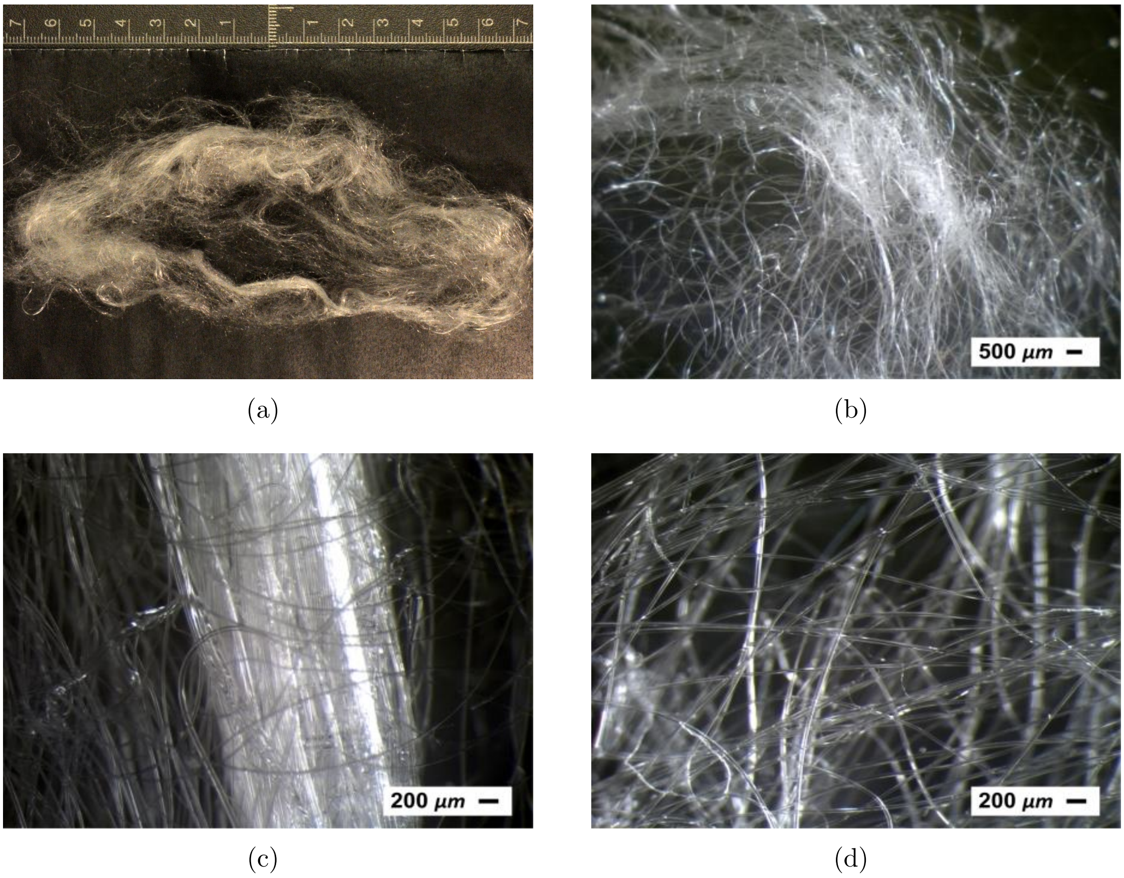
Couple of improves are made and the second mould plate is manufactured from stainless steel with similar kind design but little different dimensions. The diameter of steel mould is 5 mm smaller than the diameter of PTFE mould but also 5 mm smaller than resistor plates as a purpose to keep the spinneret ring as hot as possible. The heating capacity on the resistor edge is smaller than in the middle of the plate. Resistor flanges reduce the risk that polymer cools down before getting out from the spinneret. Also orifice diameter is made half smaller.

In the Table 4.6 is presented results of rotational melt spinning with P(L/D)LA 96/4. In general P(L/D)LA 96/4 forms fibrous floss containing several centimetres long separate fibers with different fiber diameters, see Figure 4.5(a). In first processings where rotation and heating are turned on at the same time, fiber diameters are commonly between 20-25 μm, but the diameter distribution is high. Fiber diameters vary from 5 μm to over 30 μm or 40 μm. Also fibers with diameter of 60-70 μm are formed. Processes with preheating of polymer results to little smaller average fiber diameters, varying approximately between 17-23 μm. Fiber forming temperature vary between $120 - 160\,^{\circ}\mathrm{C}$. Different collectors do not have influence in fiber diameters or significantly to the structure of the fibrous floss.

Fibers are bright coloured, mostly with round shape cross-section and smooth surface when observing by optical microscopy, see Figure 4.5. They are little curled and they entangled with each other forming a fibrous floss like structure as seen in Figure 4.5(b). Fibers are little more curled than in case of orifice band spinneret. Fiber surface faults can be seen when observing samples by SEM. Fiber fractures and transverse cracks are seen in Figures 4.6(a) and 4.6(b). Transverse cracks and tensions inside fibers make brittle parts to fibers. In Figure 4.6(c) is shown longitudinal streaks which are well-known instabilities in fiber forming process. Still reasons for forming of these instabilities are not known [28]. All samples contain beads. Usually beads are formed in the beginning of the process and they are found in the end of fibers but also beads-on-string like fibers are found. When rotation and heating are both turned on in the beginning of the process, high number of beads with short tails are formed. These needles are not elongate enough to form long fibers. But when spinneret is preheated, always up to at least 120 °C, lower number of beads and needles are formed. Processing times also shorten by several minutes. Needle formation seems to be related to the melt temperature and melt viscosity. Fibers solidify fast after formation and they are able to be handled without causing any damage to them. P(L/D)LA 96/4 fibers do not stick to the wall of collector bowl, and instead of that, fibers blow around in the bowl. For that reason fibers are collected by tweezers during the processing. Fibers entangled easily with the spinneret, almost in every processing time and fiber bundles or lumps are formed, see Figure 4.5(d). Sometimes fibers entangled on the top of the spinneret and sometimes on the bottom of the spinneret.

Table 4.6: *Optical evaluation of rotational melt spun PLDLA 96/4 fibers fabricated by stainless steel mould spinneret with tapering furrows.*

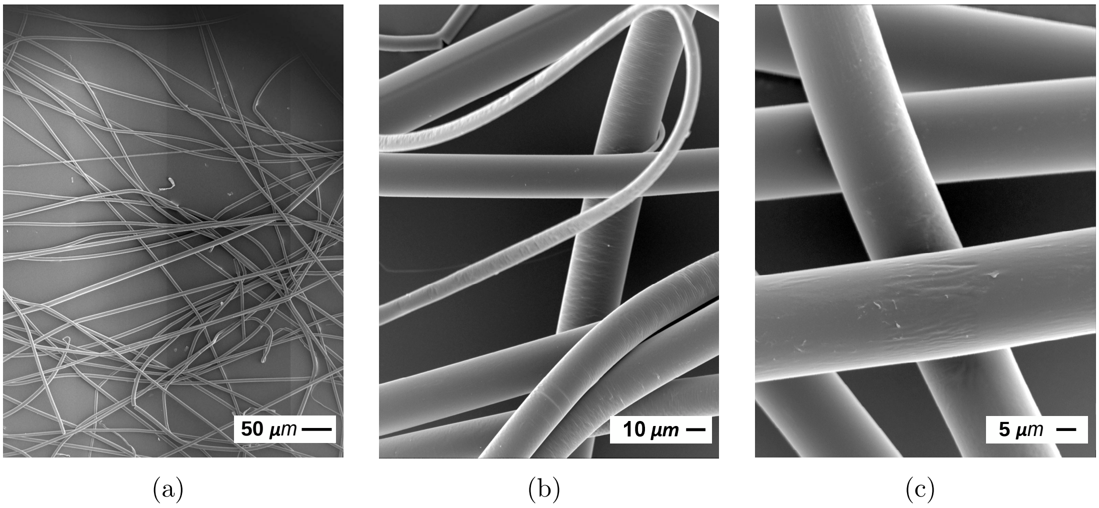
Processing	**Fiber diameters, Sample evaluation**	**Processing time and notes**
RMS_SmTf_PLDLA96/4_1	Partly burned, curled fibers Beads in the end of fibers	21:00 Fiber forming temperature 150-160°C
RMS_SmTf_PLDLA96/4_2	6-35 μm, 60-70 μm Little rough feeling material Beads with tails Not as curly as previous ones	18:00 Fiber forming temperature 120-125°C
RMS_SmTf_PLDLA96/4_3	4-40 μm, mostly 20-25 μm Fiber diameter distribution more even than earlier Some beads Quite soft feeling	16:00+ Fiber forming temperature 120-160°C Fibers entagled with the screw on the top plate
RMS_SmTf_PLDLA96/4_4	5-30μm Mostly approx. 20 μm Curly fibers	17:45 Fiber forming temperature 130-145°C Fibers entagled with the top of the spinneret
RMS_SmTf_PLDLA96/4_5	15-23μm Partly parallel fibers and partly curly fibers Even fiber distribution Beads	13:30 Fiber forming temperature 140°C Fibers did not form right after turning on the rotation Fibers entagled with the spinneret
RMS_SmTf_PLDLA96/4_6	5-25μm, mostly 20-24μm Couple of burned beads Couple beads-on-string fibers	11:45 Fibers starts to form right after turning on the rotation, 140°C Fibers entagled with the spinneret
RMS_SmTf_PLDLA96/4_7	Mostly 17-23μm	13:00 Fiber forming temperature 140°C Fibers entangled with leather ledges on the top of the spinneret
RMS_SmTf_PLDLA96/4_8	Mostly approx. 20 μm Couple of curly tangles Quite even fibers Beads in the end of fibers	approx.14:40 Fiber forming temperature 120-140°C Fibers entangled with the spinneret Bottom plate has lower temperaturethan upper plate



(a) (b)

(c) (d)

Figure 4.5: *(a) Sample RMS_SmTf_PLDLA96/4_6. A measuring line segments are in centimetres. (b) Sample RMS_SmTf_PLDLA96/4_4. Curled fibers entangle with each other. (c) Sample RMS_SmTf_PLDLA96/4_4. Fiber bundles are formed when fibers entangled with the spinneret. (d) Sample RMS_SmTf_PLDLA96/4_6. Bright and quite even sized fibers.*



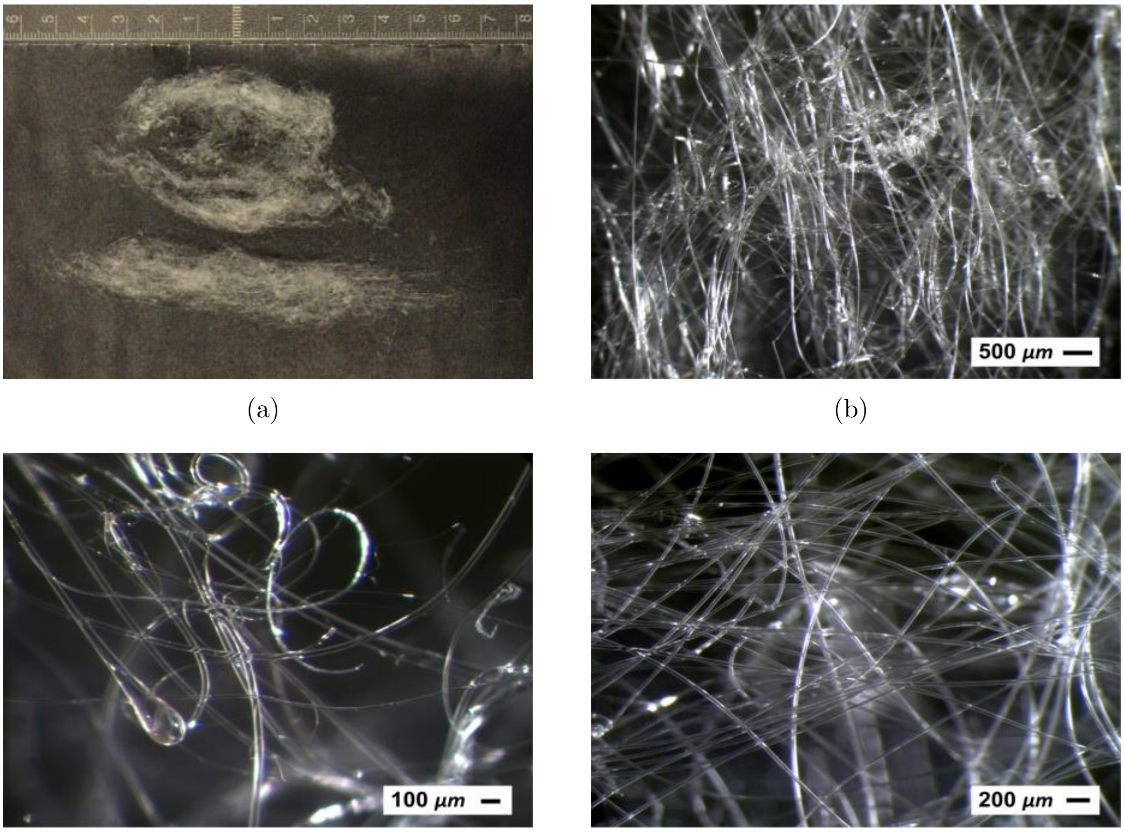
(a) (b) (c)

Figure 4.6: *Sample RMS_SmTf_PLDLA96/4_6. (a-b) Brittle fibers with quite even diameters. Transverse cracks and fiber breakages are shown. (c) Longitudinal streaks, called sharkskin instabilities, on a surface of the fiber.*

Processing of lower iv-value PDLA 50/50 is studied and results are presented in Table 4.7. When rotation and heating are turned on at once in the beginning of the spinning process first needles are formed at 75 °C and fibers at $110 - 115\,^{\circ}$C. Preheating temperature is then determined to be approximately 120 °C. End products contain different sized fibers which are unevenly distributed through the samples. Fiber diameters vary commonly between 5-25 μm and fiber lengths approximately between 2-6 cm. The bead diameters are from 100 μm to over 200 μm. When rotation and heating are both turned on in the beginning, samples contain separate beads. But when the polymer is preheated before rotation, beads are located in the end of fibers, like in Figure 4.7(c). Processing time is couple of minutes shorter when spinneret is preheated before rotation.

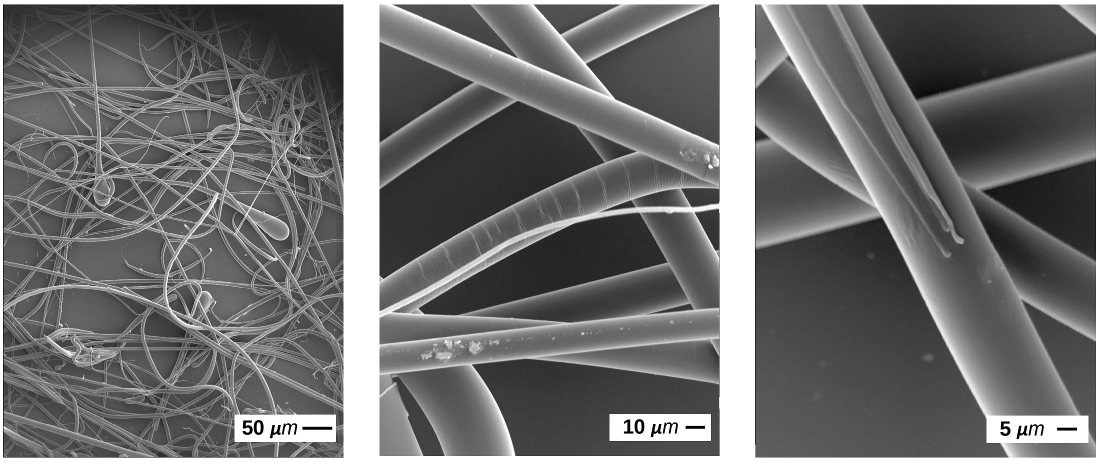
Fibers are commonly bright, round shape and they have smooth surface when observing by optical microscopy. End products are shown in Figure 4.7. Most of fibers are little curled but part of the most thinnest fibers are more curled and twisted around thicker fibers. End products contain relatively huge number of fibers which are melt together forming tangles which can be seen without any magnifying tools. Some fibers, at least in first sample, contain surface tensions which are shown as matt cracks in fiber surfaces. Those parts are quite brittle and fibers break off easily when handling them. Polymer scraps are fall off from all samples. Fiber cracks are shown in Figure 4.8(a) and transverse cracks are shown in Figure 4.8(b). Small polymeric knots and thin fibers which are stuck on the surface of fibers are shown in Figures 4.8(b) and 4.8(c).

Fibers are collected by tweezers when aluminum collector is used, but the web wall collector enables fiber collection in the end of the process. Breathable collector enables fibers to flow freely, layer on the bottom of the collector bowl and cool down. PDLA 50/50 fibers flow and settle on the bottom unlike P(L/D)LA 96/4 fibers which eddied along the air flow near the spinneret. Fibrous material is then able to be collected as airy mat or web form. The web structure is not formed when aluminum collector bowl is used due to fibers eddy along the air flow instead of settling down. Temperature inside the web wall collector is lower than inside aluminum bowl, and fibers are able to cool and solidify faster and they are not melted together as tightly as in case of aluminum collector.



(a) (b) (c) (d)

Figure 4.7: *(a) Sample RMS_SmTf_PDLA50/50_3. A measuring line segments are in centimetres. (b) Sample RMS_SmTf_PDLA50/50_1. Fibrous floss. (c) Sample RMS_SmTf_PDLA50/50_3. Fiber diameter range is high. Bead in the end of fiber. (d) Sample RMS_SmTf_PDLA50/50_1. Quite even bright fibers.*



(a) (b) (c)

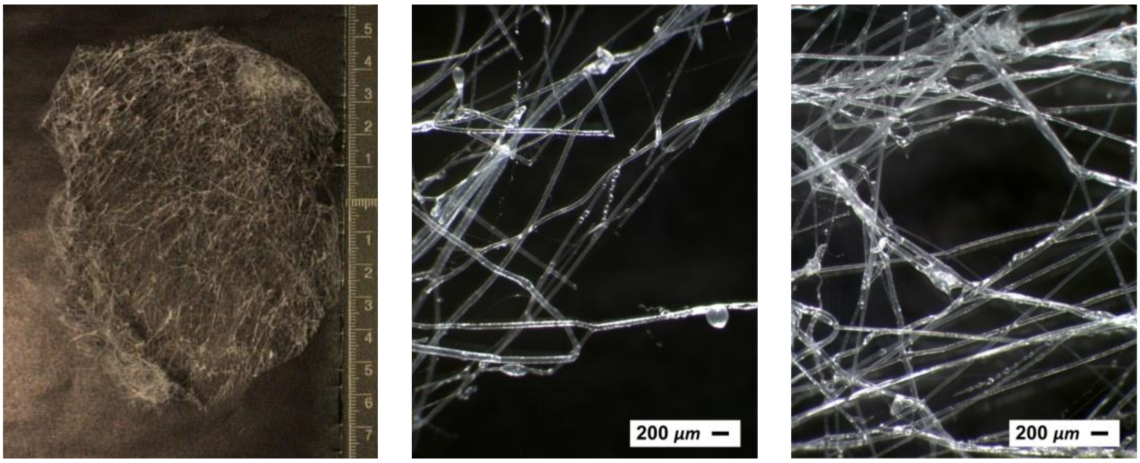
Figure 4.8: *Sample RMS_SmTf_PDLA50/50_3. (a) Elongated beads and fiber breakages and found from quite rough fibrous sample. (b) Transverse cracks and polymeric knots are shown on the surface of fibers. (c) Very thin fibers are stuck by melting on the surface of the thicker fiber.*

Table 4.7: *Optical evaluation of rotational melt spun PDLA 50/50 fibers fabricated by stainless steel mould spinneret with tapering furrows.*

Processing	**Fiber diameters, Sample evaluation**	**Processing time and notes**
RMS_SmTf_PDLA50/50_1	Mostly 18-24 μm Unevenly distributed different sized fibers Fibers curled and partly melt together Thinnest fibers entangled with larger fibers Beads Brittle fibers	15:20 Needles at 75°C Fiber formation temperature 110-115°C Fibers collected by tweezers
RMS_SmTf_PDLA50/50_2	5-25 μm Couple thicker 5-36 μm Beads 130-220 μm Large fiber diameter distribution Curly tangles Fibers partly melted together Beads in the end of fibers	14:00 Fiber formation temperature 120-140°C Fibers collected by tweezers
RMS_SmTf_PDLA50/50_3	7-24 μm Finest fibers entangled around thicker fibers Mat like end product Softer and more airy end product than before Separate fibers and some beads Easier to handle (separate fibers)	13:30 Fiber formation and processing temperature 125-170°C Fibers collected at once in the end

Results of rotational melt spinning of lower melting temperature polymer, PCL, are presented in Table 4.8. In first processing when spinneret is warmed and rotated from the beginning, fibers are formed at temperature range of $70 - 90\,^{\circ}\mathrm{C}$. Preheating temperature is determined to be approximately $90\,^{\circ}\mathrm{C}$. Unlike in all previous processings, preheating of the polymer do not shorten the processing time. The first processing lead to formation of thick fibers, with diameters of 40-70 μm. The temperature inside the aluminum collector bowl is high and fibers are not able to be collected. Part of the fibers entangle with the spinneret and fiber lumps are formed.

The second processing lead to formation of thin non-woven web structure, see Figure 4.9(a). Fibers are much thinner than in previous trial and fiber diameters vary commonly between 15-45 μm. Some fibers with diameter under 10 μm are found but mostly fibers are 20-40 μm. The web structure is able to be collected due to the web wall collector. Fibers are angular, white coloured and they have matt surface, as seen in Figures 4.9(b) and 4.9(c). The shape and the colour might be result of insufficient stretching of fibers after formation. Some bright fibers are found from the rim of the collector in second processing time. Fibers which are flown to the rim have the biggest fluctuation. The most curled and most of the bright fibers are among the most far flown fibers. Thickest fibers do not flow to the rim and they are layered on the bottom of the bowl. Beads, up to 200 μm, are formed and they are found from the middle of fibers. Beads-on-string like fibers are formed and even the most thinnest fibers contain beads in the middle of the structure. Beads seems to be formed along the whole processing, not only in the beginning.



(a) (b) (c)

Figure 4.9: *(a) Sample RMS_SmTf_PCL_2. A non-woven web structure. (b) Sample RMS_SmTf_PCL_1. Matt fibers and beads-on-string like fibers. (c) Sample RMS_SmTf_PCL_2. White, matt and angular fibers.*

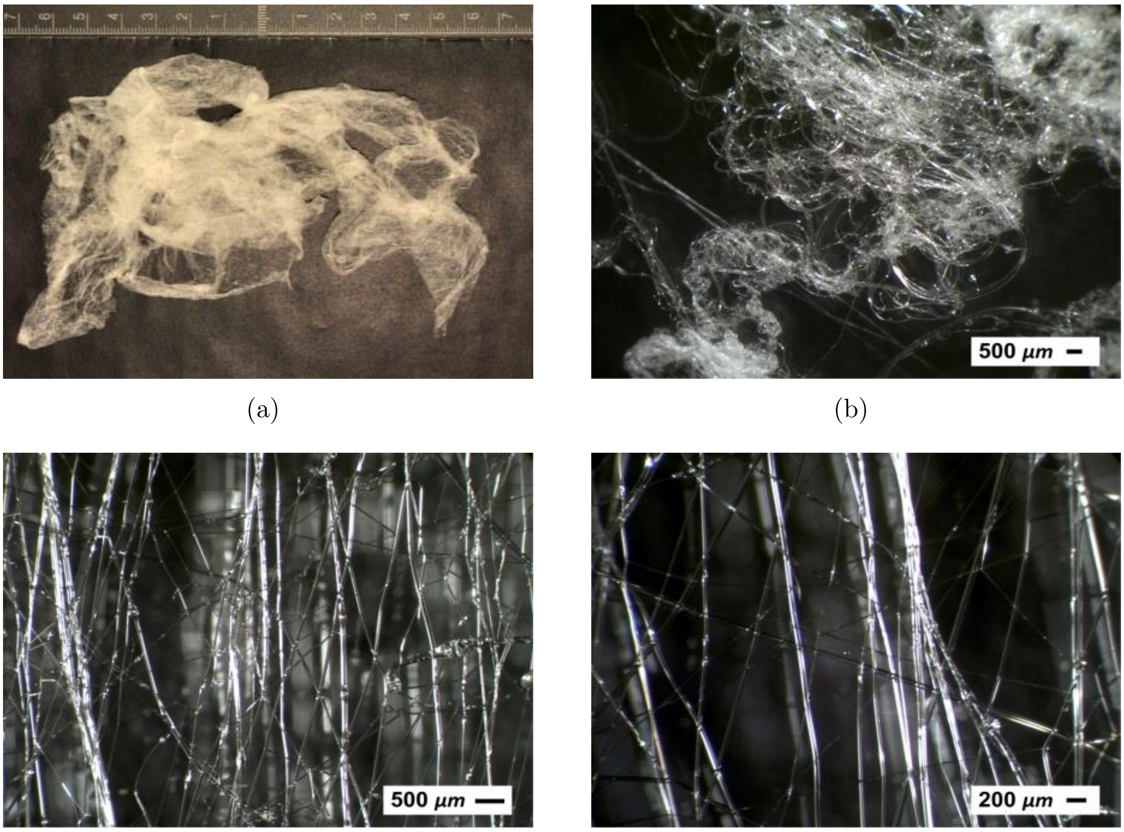
Table 4.8: *Optical evaluation of rotational melt spun PCL fibers fabricated by stainless steel mould spinneret with tapering furrows.*

Processing	**Fiber diameters, Sample evaluation**	**Processing time and notes**
RMS_SmTf_PCL_1	40-70 μm White and matt fibers Beads also in the middle of fibers Curls, tangles, beads-on-string like fibers	13:00 Fiber formation temperature 70-90°C Some fibers entangled with the spinneret and formed as lumps Fibers do not elongate enough Too hot in the collector bowl and fibers are not able to collect
RMS_SmTf_PCL_2	15-45 μm Fiber web (fibers melt together) Mostly white and matt fibers Only few longer fiber Tangles, lumps, beads in the middle of fibers	13:00 Fibers formed over 90°C Fibers collected in the end of processing Electrical safety band under the spinneret is removed before spinning Fibers do not entangled with the spinneret Fibers layered on the bottom of the bowl

Results of processing of PLCL 70/30 are presented in Table 4.9. When heating and rotation are turned on at the same time, needles start to form over 70 °C and first fibers at 120 °C. Fibers are very short and they layer to the bottom of the collector bowl. Due to low T_g of the polymer fibers do not have time to cool or they get warmer again in the aluminum collector bowl, resulting that they melt tightly together. Collection of fibers do not succeed and the end product contract when fibers are tried to detach from the bowl. In later processings spinneret is preheated up to $120 - 140$ °C and fibers are able to collect due to the web wall collector. Fibers are detached after they are properly cooled down. Fibers form web structure when little warm and sticky fibers are bedded on the bottom of the collector bowl during the spinning process. Web structure is shown in Figures 4.10(c) and 4.10(d). Handling and storing of samples are difficult because fiber web is rubbery and sticky and it contract easily, see Figures 4.10(a) and 4.10(b). Fibers stretch and the web curl and contract little when detaching from the collector.

Fiber diameters vary mostly between 10-20 μm. Preheating shorten the duration of the spinning process but also make fiber diameters smaller. The amount of fibers with diameters of under 10 μm is higher and diameter of thickest fibers decreased from 40-50 μm to approximately 30 μm when spinneret is preheated. Fibers are mostly smooth, bright coloured and glossy when observing them by optical microscopy. Some air bubbles and swelled parts are found from few fibers, like in Figure 4.10(c). SEM-images are shown in Figure 4.11. Fibers are not as straight and smooth as PLDLA 96/4 fibers but they much staighter than PCL fibers. Fiber glueing is shown in Figure 4.11(b).

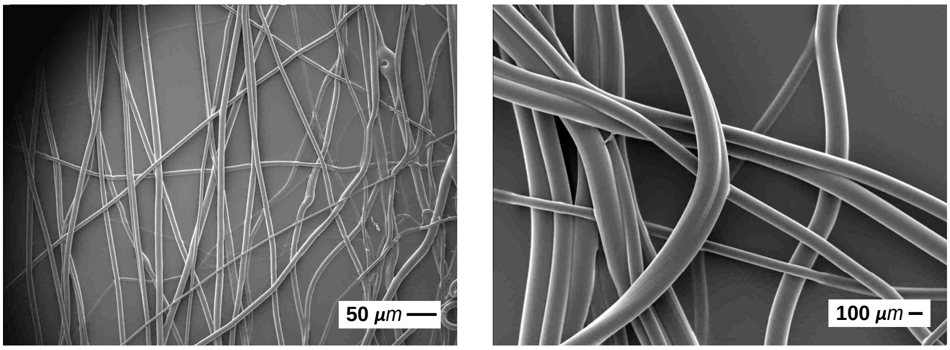
Fiber forming process seems to be critical for small changes. Preheating temperature have big influence in processing of PLCL 70/30 and even small changes of preheating temperature affect fiber formation and fiber elongation. If the temperature is little too low fibers do not elongate and instead of proper forming, fibers do not get away form the closeness of the spinneret and they get entangled with the spinneret easily. In last two processing, fibers entangled after coming out form orifices. Already formed fibers adhered to the entangled fibers, and the whole fibrous web structure get entangled and contract in closeness of hot spinneret.



(a) (b)

(c) (d)

Figure 4.10: *(a) Sample RMS_SmTf_PLCL_70/30_2. Contracted fibrous web. (b) Sample RMS_SmTf_PLCL_70/30_1. Sticky fibrous floss. (c-d) Sample RMS_SmTf_PLCL_70/30_2. Fiber web structure.*



(a) (b)

Figure 4.11: *(a-b) Sample RMS_SmTf_PLCL_70/30_2.*

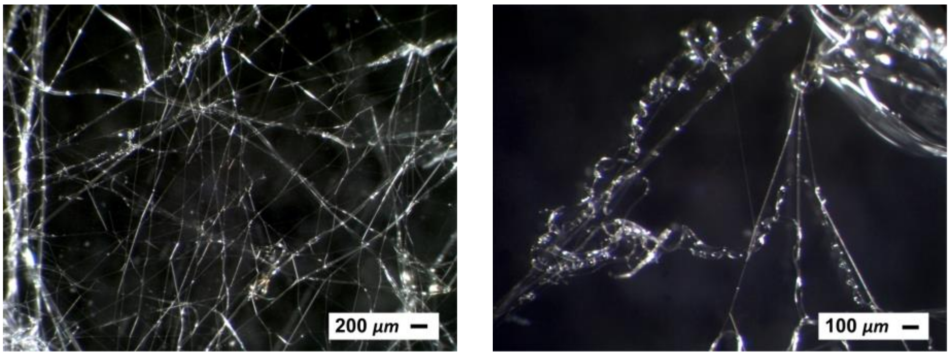
Table 4.9: *Optical evaluation of rotational melt spun PLCL 70/30 fibers fabricated by stainless steel mould spinneret with tapering furrows.*

Processing	**Fiber diameters, Sample evaluation**	**Processing time and notes**
RMS_SmTf_PLCL_70/30_1	10-20μm, some 40-50 μm Fiber web Fibers melt together Straight fibers, curly tangles, beads	16:00 Needles over 70°C Fiber formation temperature 120°C
RMS_SmTf_PLCL_70/30_2	Mostly 10-20 μm Many <10 μm, some 30 μm Transparent and glossy fibers Some air bubbles in fibers Tangles, lumps, beads in the middle of fibers Relatively huge number of thin fibers	14:00 Temperature of top plate and bottom plate differ Fiber forming at 130°C, right after turning on the rotation
RMS_SmTf_PLCL_70/30_3	Withdrawn fibrous web	13:00 Fiber formation after turning on the rotation at 117-163°C Fibers entangled with the spinneret Lumps
RMS_SmTf_PLCL_70/30_4	Withdrawn fibrous web	13:00 Fibers entangled with the spinneret Lumps Beginning of the process was more promising

4.2.3 Results with plate mould spinneret with widening furrows

Steel mould spinneret with widening furrows is studied with same polymer and similar processing patterns than the tapering furrow spinneret. Preheating is found to lead better results but still first trials are made by turning the rotation and heating on at the same time. Only web wall collector is used in these trials and electrical safety band is removed before processings.

PLCL 70/30 is the first polymer which is processed by the widening furrow spinneret and results are presented in Table 4.10. Aluminum ledges are not used under the spinneret and web wall collector is descend not until the third processing. Processing times and heating ranges are in order of processing times with tapering furrow spinneret. In first processing, fiber forming temperature is 125 °C and in later studies spinneret is preheated up to $100 - 130\,^{\circ}\mathrm{C}$. Polymer burns in first processing resulting to yellowish fibrous web which contain brown beads. Thin fibers, in diameter of 5-7 μm, form the web structure. The web contain thicker fibers, in diameter of 11-16 μm, which curled and tangled forming roughness to the web. Polymer is little burned and the sample contain brown beads. Next processing result to similar kind of web structure where thinnest fibers form the web and thicker fibers are adhered to the web. Fibers are unburned and white unlike in previous process. Fiber diameters vary from 5 to 20 μm. Thickest fibers may have plough into a bottom of the collector bowl and curled due to they do not have space to stretch. For that reason, the bottom of the web wall collector is lowered and after that modification formed fibers are little straighter and longer than in previous processings. The third sample contain huge number of thin and curly fibers. They are bright coloured and less tangled than before. Fiber diameters are mostly under 10 μm but the diameter range is 3-15 μm. Also some ribbon or film like fibers are found and the sample contain a few beads in range of 100-150 μm. The web structure is shown in Figure 4.12(a) and ribbon like fibers are shown in Figure 4.12(b). As it can be seen from SEM image 4.13(a) fibers are glued together forming fiber bundles in the web structure. The web stucture is not only a result of separate fibers which are stick together but the polymeric material is branched like in Figure 4.13(b).

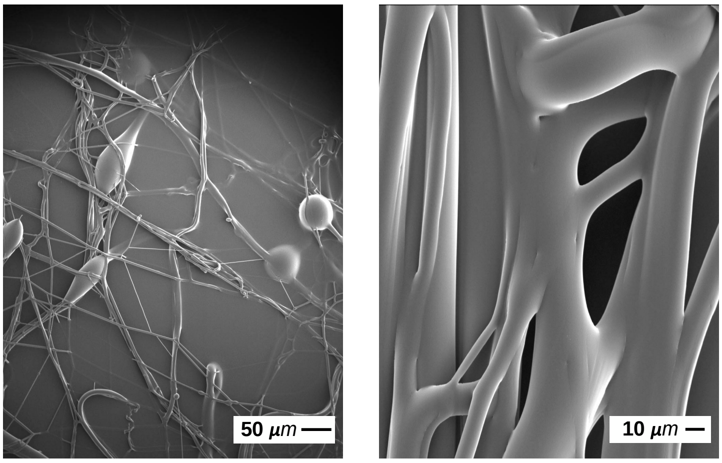


(a) (b)

Figure 4.12: *(a) Sample RMS_SmWf_PLCL_70/30_1. Fiber web structure. (b) Sample RMS_SmWf_PLCL_70/30_3. Ribbon or film like structure.*

Table 4.10: *Optical evaluation of rotational melt spun PLCL 70/30 fibers fabricated by stainless steel mould spinneret with widening furrows.*

Processing	**Fiber diameters, Sample evaluation**	**Processing time and notes**
RMS_SmWf_PLCL_70/30_1	Thin fibers 5-7 μm Thicker fibers 11-16 μm Yellowish fibrous web With thicker tangles or knots More fine fibers than before	17:00 Fiber forming temperature 125°C Temperature rose up to 175-180°C
RMS_SmWf_PLCL_70/30_2	Thin and straight fibers form web Thicker fibers which are curled Couple of brown beads fibers 5-20 μm, beads 155 μm	17:30 Fibers seems to plough into bottom of the collector bowl
RMS_SmWf_PLCL_70/30_3	Fibers 3-15 μm, beads approx. 150 μm Fibers are straighter than before Ribbon fibers are found Long fibers Less tangled fibers than ever	13:30 Fibers seems to have more space to elongate

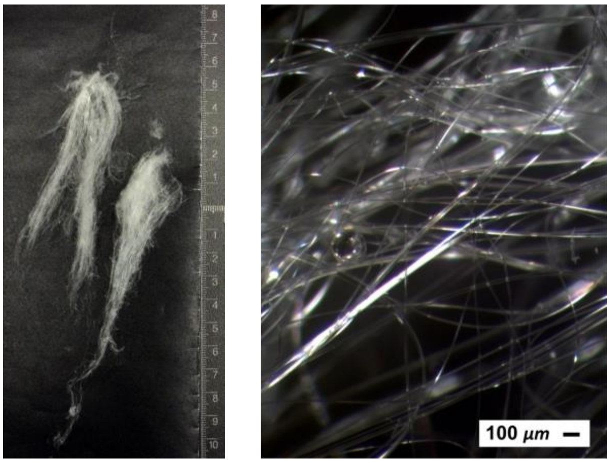


(a) (b)

Figure 4.13: *Sample RMS_SmWf_PLCL_70/30_1. (a) Fibrous web structure and fiber bundles. (b) Branched fiber junction.*

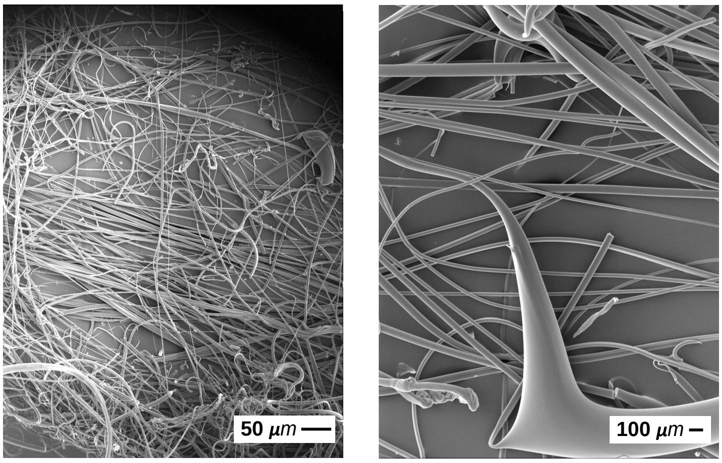
Results of processing PLDLA 96/4 with widening furrow mould spinneret are presented in Table 4.11. In first processing fibers are formed at 130 °C and in second processing spinneret is preheated up to that temperature. There is no significant difference in fiber forming temperatures when two plate mould spinnerets are compared together. Also processing times are in same range when comparing these spinnerets. SmWf has couple of minutes longer processing times. Aluminum ledges are used under the spinneret bottom to prevent fibers to eddy under the spinneret. Still fibers have to collect by tweezers and part of fibers get entangled with the spinneret and the ledges forming fiber lumps. Despite that aluminum ledges do not prevent fiber entanglement properly, they still cause stronger air flow inside the collector. Descended web wall collector is tested in the latter processing, but no remarkable difference is shown.

End product is fibrous floss containing short, few centimeters long, and quite straight fibers, see Figures 4.14. Fibers are bright coloured and more uniform quality than the fibrous material processed using tapering furrow spinneret when observing by optical microscopy. Fiber diameters vary from 4 to 15 μm in first processing and from 3 μm to 12 μm in second processing. Fiber diameters rest mostly under 10 μm when polymer is preheated in the spinneret. The amount but also the ratio of thin fibers, diameter in order of 5 μm, is higher than when SmTf-spinneret is used. Samples contain few yellowish and brownish beads. In second processing, remarkable less beads are found than samples processed SmTf-spinneret. First products which came out from the spinneret resemble ribbon or thin film. These are formed especially when spinneret is preheated before start-up of rotation. Few thicker melted parts, and fibers which are clued together, are found from both samples. As seen in SEM images 4.15 fiber breakages and melted polymer lumps are found from the sample. When comparing SEM images 4.15(a) and 4.6(a) together, it can be seen, that SmWf-spinneret result to more rougher end-products.



(a) (b)

Figure 4.14: *(a-b) Sample RMS_SmWf_PLDLA_96/4_2.*



(a) (b)

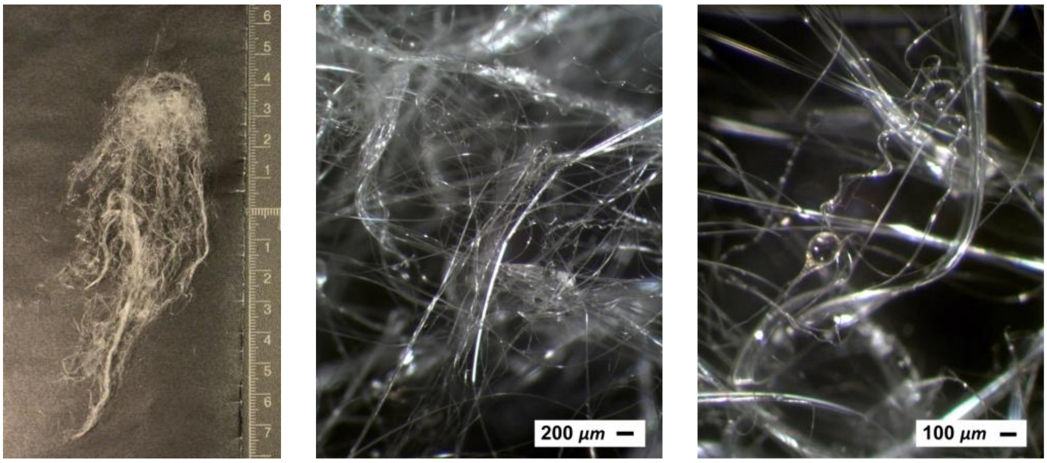
Figure 4.15: *(a-b) Sample RMS_SmWf_PLDLA_96/4_2.*

Table 4.11: *Optical evaluation of rotational melt spun PLDLA 96/4 fibers fabricated by stainless steel mould spinneret with widening furrows.*

Processing	**Fiber diameters, Sample evaluation**	**Processing time and notes**
RMS_SmWf_PLDLA_96/4_1	Bright fibers	20:00
	Most even of quality fibers than before	Fiber formation after at 110-130°C
	4-15 μm	Part of fibers entangled and form lumps
	Higher number of thin fibers than ever	
	Few beads, couple of yellowish	
RMS_SmWf_PLDLA_96/4_2	Short round shape fibers	17:00
	3-12 μm, mostly under 10μm	Fibers entangled and form lumps

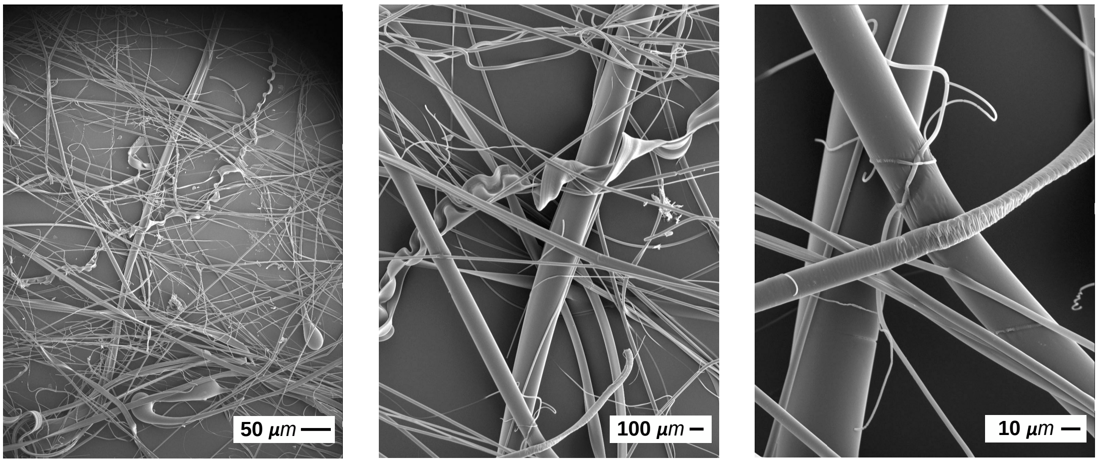
Results of processing PDLA 50/50 with the widening furrow spinneret are presented in Table 4.12. Little shorten and downward leading, 0.5 cm long aluminum ledges, are fixed under the spinneret in both processing times. Fibers do not entangle with the spinneret and aluminum ledges seems to work properly. Lowered web wall collector enables fibers to settle on the bottom of the collector bowl and they are picked up all at once. Fiber forming temperature is $100 - 110\,°\mathrm{C}$ in first processing and spinneret is preheated up to 125 °C in second trial. Processing durations are couple of minutes longer compared to processing times with SmTf-spinneret.

End products are spacious felt with thickness of a few millimeters, see Figure 4.16(a). Fiber diameters vary between 4-14 μm in both samples but the diameter distribution is quite high. Different sized fibers entangle with each other, like in Figure 4.16(b). Some fibers are melted together and wavy ribbon fibers, 25 μm in width, are found from samples, like in Figure 4.16(c). Fibers are mostly bright coloured but the second sample is little yellowish which indicates burning of the polymer. Some bright and some brown beads are found from samples. SEM-images are shown in Figure 4.17. Fiber breakages, melted polymer lumps and transverse cracks on fiber surfaces are found from the sample.



(a) (b) (c)

Figure 4.16: *Sample RMS_SmWf_PDLA_50/50_1.(a) Spacious fibrous floss. (b) Different sized fibers tangled with each other. (c) Film like ribbon.*



(a) (b) (c)

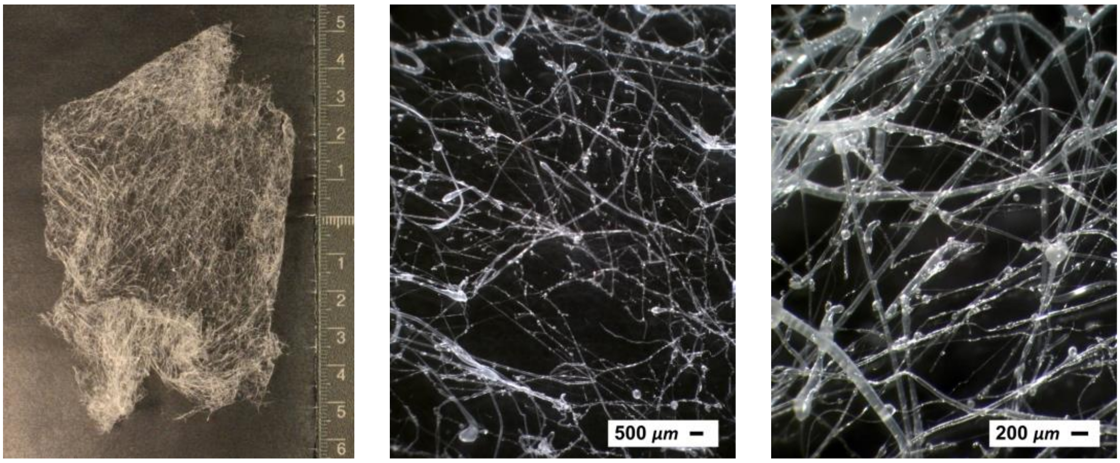
Figure 4.17: *(a-c)Sample RMS_SmWf_PDLA_50/50_1. Rough fibrous floss with fiber breakages, melted polymer lumps and transverse cracks on fibers.*

Table 4.12: *Optical evaluation of rotational melt spun PDLA 50/50 fibers fabricated by stainless steel mould spinneret with widening furrows.*

Processing	**Fiber diameters, Sample evaluation**	**Processing time and notes**
RMS_SmWf_PDLA_50/50_1	Fibers 4-14 μm, 6-8 μm quite general Ribbon type fibers and beads are formed Spacious mat Rough appearance, fractured fiber pieces and tangled fibers	18:00 Fiber forming temperature 100-110°C Aluminum ledges under the spinneret works properly
RMS_SmWf_PDLA_50/50_2	Fibers 4-13 μm Ribbons 25 μm wide Bright, round shape fibers with larger diameter distribution than PLDLA 96/4 Spacious mat	16:00 Fiber forming temperature 150°C

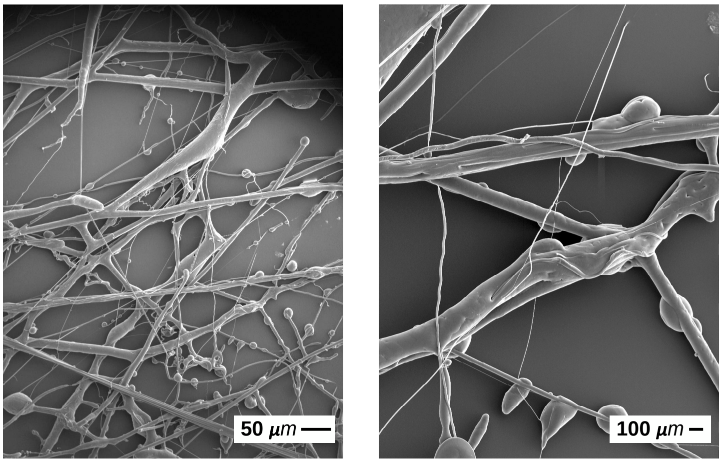
PCL is processed twice with the mould spinneret with widening furrows and results are presented in Table 4.13. Fibers are let to settle on the bottom of the lowered collector bowl and they are picked up at once in the end of the processing. First fibers come out at 70 °C and thin fibrous web was layered slowly on the bottom of the collector bowl. Fibers do not flow long and fiber forming is difficult to distinguish by eye. In preheating process, spinneret is heated up to 75 °C before turning the rotation on. Due to difficult distinguishing of fiber forming, processing times are over long to make sure that all polymer comes out from the spinneret. Processing times are for that reason 5-10 minutes longer than in case of SmTf.

End products are thin and fragile webs which rib easily, see Figure 4.18(a). The first web is little thicker than the second one. Fibers are under three centimeters long. These PCL samples contain maybe the most thinnest fibers which are ever produced by the device but the fiber diameter distribution is high. Fiber diameters vary mostly between 2 and 15 μm, but also thick fibers with diameters up to 50 μm are formed. Fibers are white coloured and branched. Many beads and bead-on-string fibers are formed, but ribbon fibers are not formed. Bead diameters vary from 6 to 200 μm. Web structure and beads are shown in Figures 4.18(b) and 4.18(c). As seen from SEM-images, Figure 4.19, smooth fibers are not formed but rough and lumpy fibers and huge number of beads are formed.



(a) (b) (c)

Figure 4.18: *(a) Sample RMS_SmWf_PCL_1. Non-woven web. (b-c) Optical microscopy images from web structure.*



(a) (b)

Figure 4.19: *(a-b) Sample RMS_SmWf_PCL_1. SEM-images where rough fibrous web structure is shown.*

Table 4.13: *Optical evaluation of rotational melt spun PCL fibers fabricated by stainless steel mould spinneret with widening furrows.*

Processing	**Fiber diameters, Sample evaluation**	**Processing time and notes**
RMS_SmWf_PCL_1	Thin web from short fibers	25:00
	Fibers 2-50 μm, mostly under 20 μm	Fiber forming at 70°C
	Beads 6-200 μm	
	Branched white fibers	
RMS_SmWf_PCL_2	Thin stretching fiber web	19:00
	White branched fibers	Fiber forming 70-80°C
	Fibers mostly 2-15 μm, some up to 50 μm	
	Many beads-on-string fibers	

4.2.4 Overall results of rotational melt spinning

In summary, rotational melt spinning technique is studied with one commercial device, three different spinnerets and four thermoplastic polymers. Different processing variations are studied and the effect of different processing parameters are evaluated. RMS result fibers with diameter range generally from 5-15 μm. Fiber diameters rest bigger than originally desired. Separate fibers and coarse non-woven webs are formed depending on the used polymer. The process is not repeatable and the quality of fibers is uneven. End-products contain mostly round shape fibers. The device and processing parameters need further optimization due to fibers contain relatively huge amount of faults.

End-products contain beads, ribbons or film-stripe fibers, swelled fiber, curls, tangles and melt glued fiber bundles. Polymer knots and lines are found from surface of fibers. Fiber breakages exist and part of the fibers are fragile containing transverse cracks. Transverse cracks and fiber breakages are shown e.g. in Figures 4.6(a), 4.6(b) and 4.8(b). Surface faults are shown 4.6(c) and small knots in Figure 4.8(b). Film-stripe fibers, beads and defective stretched fibers are shown in Figures 4.17(b) and 4.13. Branched fiber structure is shown in Figure 4.13(b) and melt glued fibers are shown in Figure 4.8(c).

Device

The existing device set boundaries to rotational melt spinning of polymers. A structure and a size restrict the design of the spinneret and limit possibilities to affect processing parameters, like rotation speed. The apparatus is quite small and for that reason, it is not possible to fix a large or heavy spinneret on it. This apparatus has no power to rotate heavy spinneret. The size of the device limit the rotation speed of the spinneret. The constant rotation speed of the rotor is 2800 rpm and it is considered to be increased, but the speed up is not carried out due to in this scale machine the durability or bearings restrict it. Bearings may wear out.

The slow rotation speed seems to be the most limiting parameter in this study and the most limiting feature of the device. Rotating motion brings about centrifugal force which push the polymer melt out from the spinneret. The strength of the force is related to the rotation speed and the slower the rotation speed, the smaller driving force in fiber forming, but also the weaker air flow surrounding the spinneret. All these together cause insufficient flowing and stretching of fibers which result to large fiber diameters. Rotation speed has also influence in the standard deviation of fiber diameters [32]. Slower rotation speed causes wider standard deviation [32]. According to that the increase of rotation speed would result to more homogeneous end product and more equal fiber diameters. Fiber diameter distribution is quite high in all samples which are processed by the existing device. The speed up of rotation would be usable upgrade for the device and it would improve the quality of end products. Due to unchangeable rotation speed, the effect of different rotation speeds are not been able to study in practice.

Rotation speed is related to the material properties of melted polymer. High molecular weight polymers have high melt viscosity and they need higher rotation speed than low molecular weight polymers to stretch the polymer in fiber form. When comparing the rotation speed of existing device to rotation speeds presented in literature review, the existing device has too low rotation speed for processing of many polymers. Literature values vary up to 12,000 rmp or even 25,000 rpm [2; 18; 23; 37]. Material properties are discussed more later but the rotation speed and material properties together, have the biggest influence in fiber blowing. Fiber blowing is determining factor in formation of end products and in fiber collecting methods. Like in this study, fibers do not blow far from the spinneret and they are settled on the bottom of the collector bowl. Fibers are then able to entangle with the spinneret easily. But like in commercial spinning machines used in Forcespinning$^{\mathrm{TM}}$ technique, fibers blow much longer and they are able to collect on the collector walls. Fibers stick together and form web structure, and spinneret caused heavy air flow prevent the web to collapse. Collecting methods are discussed more detailed later.

Spinneret design

The effect of the spinneret design to the spinning process and to quality of end product are studied. The inner geometry of the spinneret has an influence in melting of polymer and drifting of the polymer melt, as for the outer geometry of the spinneret affect fiber blowing by affecting the flow field surrounding the spinneret. The outer geometry of the original orifice band spinneret is cylindrical, but on the top of the spinneret there are two protruding leather ledges. The reservoir of the spinneret is open from the top and when the spinneret is rotating, the air flow is directed through the spinneret by going into the spinneret from the top and flowing out through the orifice band walls. Leather ledges prevent the formed fibrous material to rise up to the spinneret and heading into the reservoir along with the substituted air. Couple of fibers entangled with these ledges. Fiber eddying under the spinneret is not a problem with the orifice band spinneret as it is with mould spinnerets. The flow field differ in case of mould spinnerets due to closed polymer reservoir.

The inner geometry of the orifice band spinneret has many disadvantages related to the processing of polymer. End products are in general burned, and formed fibers are thick with large diameter distribution. In orifice band spinneret, polymer is melted on the surface of the tube resistor which is placed in a ring of the spinneret and polymer should be melted within passing the resistor. Improper melting of polymer, uneven melting and insufficient viscosity decrease, result material lost when too viscous polymer extract from the spinneret without being able to stretch into fiber form. Usually proper melting of polymer requires longer melting time. For melting polymer in orifice band spinneret, high temperatures of the resistor is required, which easily results to burning of the polymer.

Open reservoir and geometry of orifices are not suitable for polymer processing. Open reservoir expose the polymer to oxygen and when the reservoir is heated, conditions in the reservoir enhance the polymer degradation. Open reservoir causes low pressure environment and when polymer is heated air bubbles are mixed to the polymer melt. Either the geometry of openings is not optimal and openings are too large compared to the rotation speed of the spinneret. The diameter of the orifice is 1.1 mm, when the desired fiber diameter is less than 5 μm. This means that the fiber diameter should get over 200 times smaller. The length of the orifice is only 0.5 mm which means that to ratio of the length to diameter is approximately 0.45. The optimal ratio is studied to be higher, in range of 2-10 [31]. Higher ratio of length to diameter is required to achieving polymer chain orientation. Polymer chains do not orient when the stream goes through orifices and for that reason fibers are not able to stretch in desired scale.

When new spinnerets are designed, dimensions and the weight of the spinneret is tried to keep in minimum. Outer geometry of the plate mould spinnerets are quite similar to the geometry of the orifice band spinneret, but diameters of mould plates are little smaller as a purpose to lighten the weight of the spinneret. The closed reservoir change the motion of air flow surrounding the spinneret resulting that the shape of the flow field differ from the flow field surrounding the orifice band spinneret. The air flow does not blow through the spinneret and the situation resembles a rotating solid plate. The rotating spinneret cause arching flow field, which curve from the middle of the spinneret towards the top and the bottom [1]. The curvature affect fiber blowing. Fibers, especially from PLDLA 96/4, eddy easily first upside but then more often underside of the spinneret. This drift of fibers is tried to prevent by small ledges under or the other side of the spinneret. Leather ledges on the top of the spinneret do not work, because fibers entangled with them. Longer aluminum ledges on the bottom of the spinneret cause entanglement of fibers but on the other hand, ledges seems to intensify the air flow. As for shorter of aluminum ledges on the bottom of the spinneret seems to work. Fibers do not eddy under the spinneret as easily. To proper designing of outer geometry of the spinneret, aerodynamics should study better. The further optimization of the outer geometry could enhance fiber stretching. One potential experiment to develop the spinneret design to enhance fiber stretching by directing the air flow, would be an addition of round shape screen plate on the top of the spinneret. The screen plate would contain holes which are placed in even distance from the edge and the plate would be placed on the spinneret by leaving a small cavity between the top of the spinneret and the plate. This kind of component is used in cotton candy machine which is used in the study of Huttunen et al. [23]. Additionally the spinneret design could be improved by decreasing the number of spinneret nozzles from four to two, as a trial to prevent fibers to hit together too fast after formation.

There are two variations of the plate mould spinneret with tapering furrows and one variation with widening furrows. All these spinnerets have closed reservoir and four furrows as nozzles, which end up to small openings. As an advantage of mould spinnerets compared to the orifice band spinneret is that the heating system is more efficient. Whole spinneret is heated instead of using local heater and the design of the spinneret enables heating from both sides of the mould. The heat is evenly distributed resulting to more constant and proper melting of polymer. As an disadvantage, there is no a thermoelement integrated into the device and the temperature of the closed reservoir is not possible to measure, at least when the spinneret is rotating. Other disadvantage is that rotation motion cools the ring of the spinneret and decrease the temperature of orifices. Although the surface temperature of the spinneret can be used as suitable estimation for the inner temperature of the spinneret. The mould spinnerets have closed reservoir which enables only batch processing. The amount of processable material is determined in the beginning of the spinning and polymer is not able to add during the processing. The geometry of the spinning machine or the distance between voltage tenons determines the diameter of the reservoir. The reservoir is made as large as possible but the size is still small, approximately 4.4 cm^3. Only small amounts of polymer are able to be processed in time. Closed reservoir protect the polymer from the effect of oxygen which enhance polymer degradation especially at elevated temperature. Also heat loss is smaller with the closed reservoir and lower resistor temperatures are able to use. As a further development of the device and the spinneret, proper temperature control system and an establishment of nitrogen atmosphere, would be major advantages.

The effect of nozzle geometry to the quality of end products is studied with tapering furrow spinneret and with widening furrow spinneret. Nozzle spinnerets are designed to induce elongation of the fluid and orientation of polymer chains in polymer melt. Furrows cause contraction of polymer flow [24]. In contraction flow, polymer melt flows from a larger diameter capillary into a smaller capillary. In the fluid, higher shear values present near capillary walls. An external flow occurs near the centerline of the stream and near the contraction plane. Material then stretched along streamlines and elastic stress occurs in the polymer stream. When the polymer flow through the capillary, the elastic stress partially relaxes and residual elasticity recovers when the polymer emerges from the spinneret. [24] The recovery of the elastic stress cause swelling of the polymer stream right after emerging from the spinneret. The intensity of the die swell is in relation to the ratio of the length to the diameter of the orifice. [43]

Based on this knowledge, orifice designs of each spinnerets needs to be improved. Ratio of the orifice length to the diameter is not in sufficient level in case of each spinneret. Polymer stream is not able to stretch in orifice capillaries and initial fiber diameters with the die swell factor are large. Fibers are not able to be stretched enough after formation. When comparing this method to the melt blowing technique, where polymer is feed with low rate through the nozzle and stretch into nanofiber form using hot air blow, it is shown that the strength of the air flow in case of the existing rotational melt spinning device is not strong enough. In melt blowing the nozzle diameter is smaller, at least diameter of 0.125 mm is reported to be used to fabricate fibers in average diameter of 300 nm, and the speed of the heated air flow can vary between 170-270 m/s [14; 34]. These values can be compared to the equivalent values of rotational melt spinning technique. The spinneret is rotating at speed of 2800 rpm, which means that the speed of the orifice in the ring of the spinneret is only 16.7 m/s. Additionally the flowing air is not hot and fibers solidify faster.

In general both spinnerets result to approximately similar end products but differences are found in closer inspection. Widening furrow spinneret resulted to thinner fibers than the tapering furrow spinneret which most probably is result of orifice size instead of the nozzle geometry. Openings are five times smaller in vertical direction and the final construction bathway is longer compared to tapering furrow spinneret. Long gap opening do not result to branched fibers like wanted but mostly round fibers with high degree of irregularities and roughness, like beads, polymer clumps, clumps with many tails and ribbon type curly fibers. Although fiber diameters are little smaller when widening furrow spinneret is used, the tapering furrow spinneret result to better quality end-products. Tapering furrow spinneret result more even fiber diameters and more homogenous end-products. The round shape orifice geometry restrict the emerging of the polymer also in horizontal direction, resulting better orientation of polymer chains, round shape fiber diameters and more even fiber diameters than widening furrow spinneret. However the spinning holes have too large diameter.

Dimensions and the nozzle geometry have reported to have influence in onset of instabilities of polymer flow, like melt fracture and draw resonance [35; 28]. The formation of all instabilities and fiber fault are not been able to explain but they are highly dependent on the nozzle geometry as well as material properties and output rate of fibers. [35; 28] Rotational melt spun fibers contain relatively huge number of fiber faults. Melt fractures and shark skin like lines are found from fibers. Melt fractures exist when polymer accelerate from wide diameter barrel to a narrow diameter capillary or orifice [28]. Different nozzle geometry would partly affect the formation of instabilities.

Processing parameters, heating and cooling

Processing temperatures has shown to have influence in end-products. As a limitation of the existing device is that a thermoelement is not integrated into the device and temperature adjustment and measurement are both suggestive. The temperature adjustment is carried out by regulating voltage input of resistors using the scale from 0 to 10. The temperature is measured by infrared-thermometer only from surface of the spinneret. As a future development, to ensure better repeatability of process, a thermoelement with accurate temperature adjustment should be integrated into the spinning device. Now the existing temperature measurement method gives no information about the inner temperature of the reservoir or the temperature of the polymer melt. Resistors seems to warm up reproducible in same way but controlling of temperature value is not repeatable. Defective melting of polymer granules but also burning of the polymer are difficulties of the processing.

In ideal situation, the spinneret is heated up with external heaters, like IR-heaters, which are not fixed to the spinneret and rotated with it.

Different heating functions are studied and it is shown that heating temperature and heating time have influence in polymer viscosity and fiber formation. Efficient and rapid heating is found out to be the best alternative. Preheating of the spinneret enables proper melting of the polymer and sufficient viscosity decrease before rotation. That decreases material loss but also shorten the processing time and reduces polymer degradation. As low processing temperature as possible is desired to prevent thermal degradation of polymers. By altering processing temperatures and heating times, it can be affected the quality of end-product like bead formation and fiber stretching. Low processing temperature causes beads and beads-on-the-string like fibers but also thick fibers with great diameter fluctuation. Beads-on-the-string like fibers are formed when the viscosity of the polymer melt is low enough to fiber formation but where the surface tension still resist stretching of the polymer. When the rotation and heating are turned on at the same time, separate beads and needles are formed. Preheating of the spinneret descend the number of needles and instead of forming of separate beads, beads are located in the end of fibers. Even small changes in heating process can result to significantly different end-products like when comparing samples RMS_SmTf_PLCL_70/30_2 and RMS_SmTf_PLCL_70/30_3 to each other (Tables 3.15 and 4.9). Both times polymer is preheated before rotation and there is not much variation in processing parameter. The former processing result to non-woven web which is collected after formation. At the later processing, the rotation is turned on only a little earlier which result to that the polymer is too viscous to stretch and flow after emerging from the orifice. Fibers entangle with the spinneret and the whole sample is withdrawn.

After fiber formation, fibers are cooled down and solidified. The cooling process is as critical as the heating process and it affect the structure of end-product. Too rapid cooling cause premature fiber solidification and defective fiber stretching. Significant temperature decrease right after polymer emerging from the spinneret may cause fast solidification of the fiber surface, which later may result surface cracking and other faults to fiber surfaces. Separate fibers are able to collect if polymer stream is solidified before getting contact with others. If fibers are collected when they are still warm and their surfaces are soft, fibers are melt glued together and form non-woven web structure, like in case of PLCL 70/30 and PCL. Warm collecting temperature hinder collection of fibers with low T_g. A few PLCL 70/30 samples are melt glued on the bottom of the collector bowl and withdrawn due to too warm collecting temperature.

Collectors and collecting of fibers

Collecting method and collectors are as important as the design of the spinneret. Fibrous end-product is a combined result of fiber forming and fiber collecting. Fiber flowing has great influence in collecting method. The existing device has low rotation speed which restrict fiber flowing and fibers are layered near the spinneret on the bottom of the collector bowl. Heavy fibers, especially thick PCL and PLCL 70/30 fibers which are not stretched, are settled in layers forming a flat web structure. When aluminum collector bowl is used, the temperature inside the collector rise up so high that PLCL 70/30 fibers are not able to extract from the bottom. PDLA 50/50 and PLDLA 96/4 fibers have to be removed from the collector bowl during the spinning process or they are drift and entangled with the spinneret. When fibers are collected into a breathable web wall collector, PLCL 70/30 fibrous web can be removed after proper cooling. Also PDLA 50/50 fibers are able to collect all at once in the end of the processing as an airy sheet of fibers instead of fibrous wads. Breathable walls decrease the temperature inside the collector but also prevent the formation of counter air flow to the flow caused by the spinneret. The bottom plate of the web wall collector is descent to lower level which seems to give fibers more space to stretch and more time to solidify. Still fibers do not flow far. Curled fibers, bundles, knots and tangles may be partly result of fiber ploughing into the bottom of the collector.

In Forcespinning^{TM} fibers are collected on parallel vertical sticks which are located within even distance from the spinneret [39]. Fibers are touched to the surface of the collector sticks and later formed fibers are then attached to them. Only long fibers are attached on the sticks and short fibers, needles and beads formed in the beginning of the spinning fall off. Air turbulence prevent the fiber matt to collapse. Air flow cause strain to fibers and they may stretch even when they are touched with the collector sticks. Fibers are not as tightly glued together as they were if they are layered on the horizontal plane and the end-product is more equal quality. The rotation speed of the spinneret and kinetic energy of fibers are higher than in case of the device used in this study and due to that, this kind of collecting method can not be applied in this study. Fibers do not reach the sticks.

Some fibers, especially PLDLA 96/4 and PDLA 50/50 are picked up from the collector by tweezers. Three dimensional structure is formed when tweezers are rotated about their axis and fibers are layered around the tweezers. Fibrous sheet is formed when tweezers are not rotated but fibers are just picked up from the collector. The amount of processable polymer affect the thickness of the end product. The existing device do not enable processing of large amount of polymer at time. Most clearly this is shown when PCL and PLCL 70/30 are spun and non-woven webs full of holes are formed.

Material properties and sugar

Material properties are critical for succeeding of the rotational melt spinning process. Semi-crystalline or amorphous polymers have viscoelastic nature which affect melting behaviour and fiber formation as well as properties of end-product. Polymer melting take time and in melting process polymer soften first at glass transition temperature but crystals melt not untill the melting temperature is reached. After reaching the melting temperature, the viscosity decreases and polymer chains are able to reorganize. Inherent viscosity of polymers affect the value of melt viscosity [36]. The lower iv-value, the lower melt viscosity. Inherent viscosity correlate with polymer chain lengths and among the polymer crystallinity, it has influence in fiber stretching. Polymer chains have to be long enough to be able to entangle with each other and form fibers.

Semi-crystalline PLDLA 96/4 has the highest melting range and highest iv-value (2.13 dl/g) and it result to the most smoothest fibers and to the most constant fiber diameters. Fiber diameter distribution is smaller than other polymers which shows that certain degree of crystallinity ease fiber formation and result to more homogenous end-product. In general, PLDLA 96/4 result to separate bright fibers or fibrous floss with fiber diameters varying between 5-15 μm. Amorphous PDLA 50/50 has lower melting range and iv-value of 1.52-1.52 dl/g. It result to very similar end-products to PLDLA 96/4. Fiber diameters vary generally between 5-15 μm but the standard deviation of fiber diameters is higher and more beads and roughness are formed. This shows that that polymer chain length has influence in fiber forming. PCL is semi-crystalline polymer with iv-value of 1.06 dl/g. Elastic polymer do not elongate into fiber form like polylactides. Low iv-value reflects shorter polymer chain lengths and it is shown as unevenness of end-products and bead formation. Fiber stretching is the most determining problem when PCL is processed using the existing device. Insufficient stretching result to white coloured fibrous material with many beads, bundles, polymer clumps and beads-on-string like fibers. Fiber diameters vary between 5-15 μm but diameters up to 50 μm are found and fiber diameter fluctuation range is largest when comparing all four studied polymers. Despite of poor quality of fibers, PCL form a rough non-woven elastic web. PLCL 70/30 is semi-crystalline, elastic and rubbery like polymer with iv-value of 1.5-1.6 dl/g. Compared to pure PCL, higher iv-value reflects longer polymer chains which ease fiber formation and elongation. PLCL 70/30 result to bright fibers with most thinnest average fiber diameters, under 10 μm. PLCL 70/30 result to non-woven web like PCL but fibers are smoother and less beads are found. Elastic recovery and withdrawn of fibers are problems with PLCL 70/30.

Huttunen et al. have studied the optimal iv-value for rotational melt spinning of sub-micron fibers to be in range of 0.8-1.2 dl/g [23]. Polymers with initial iv-values of 5.16 dl/g and 1.6 dl/g are used in the study. Higher iv-value polymer result to formation of flakes, when the lower iv-value polymer result to formation of fibrous floss. High iv-value correlate with high melt viscosity and resist the nanofiber formation. Inherent viscosity values are decreased during the spinning process reaching values less than one. No monomer is created during the processing which shows that the process is robust enough. [23] In this study iv-values after fiber formation are not studied but it can be conclude that polymer melting process has been harsh and degradation of polymer has occurred. Inherent viscosities of polymers are decreased and monomers are created at least in many processings. Further optimization of heating process is needed and proper thermometer is required.

It is shown that some degree of crystallinity is necessary for production of stretched fibers and improve the quality of end-product. Totally amorphous polymers do not elongate enough. This can be seen e.g. when semi-crystalline PLDLA 96/4 forms smoother and more homogenous fibers than amorphous PDLA 50/50. On the other hand, average fiber diameters are bigger in case of PLDLA 96/4. Semi-crystalline PLA has higher shear viscosity in melt than amorphous PLA [19]. A resistance to flow decreases while the rate of shear stress increases. The phenomenon is called shear thinning and it means that the increase of shear stress makes the melt more fluent. E.g. an increase in temperature leads the decrease in the shear viscosity. [19] More fluent melt result to smaller fiber diameters. The shear stress can be increased also by increasing of external pressure. The melt pressure could be increased and that way decrease fiber diameters by increasing rotation speed or applying external pressure. The crystallinity of rotational melt spun fibers is not studied in this work but the inner structure of fibers can be tried to determined by other fiber forming methods like high speed spinning, extrusion and melt blowing. In traditonal melt spinning processes, as spun fibers have usually random orientation of molecular chains when the crystallization and the formation of inner structure of fibers is formed under drawing. [35; 43] In rotational melt spinning fibers are stretched under the influence of air flow. In this study, the impact of the air flow is quite weak due to slow rotation speed of the spinneret. Most probably, the crystallization of fibers is incomplete when the external drawing stresses are not sufficient. Polymer chains might rest in not organized form before solidification which affect fiber diameters and die swell by increasing them. At the same time fiber strengths are lower.

Granule size of polymer does not show to have big influence in the processing in this study due to major differences in granule sizes do not exist. In general PLDLA 96/4, PDLA 50/50 and PLCL 70/30 have granule size in same scale with each other, when PCL has a granule size of approximately two times the size of PLDLA 96/4 granules. Bigger granule size cause that smaller amount of polymer is used in time. Polymer grinding would would increase the material volume but also result to more even melting. Especially when rotating spinneret is heated, smaller granule size would be beneficial. Also shorter processing times can be achieved. Processing of granules turned out to cause material loss when partly melted granules emerged from the spinneret but the same problem would be in case of ground polymer. The most challenging situation is when orifice band spinneret is used. As an option to maximize the amount of processable polymer and to avoid the material loss, polymer granules can be compression moulded into button shape. The compression moulding as a preliminary stage to rotational melt spinning is not studied but additional heating step during the processing increase the risk of polymer degradation. To extend the diversity of end products, mixing of two polymers during the spinning process is considered. Polymer grinding or compression moulding would be useful in that case.

The existing device is designed for processing of sugar but material properties of sugar differ from properties of polymers. Sucrose is a hard crystalline material which exist in lump or powder form. It is di-saccharide composed of glucose and fructose and the chemical formula of sucrose is $C_{12}H_{22}O_{11}$ [30]. It is combustible and decomposes at $160 - 186\,°\mathrm{C}$. [30] Melting behaviour and melt properties of highly crystalline sugar differ from melt properties of viscoelastic polymers. Sucrose has one melting point at which solid crystals are melted and material is liquefied. [3; 40] Viscosity of the melt decrease rapidly. Melted sugar has lower viscosity level than polymers and molecular chains can pass each other and shape transformation occurs more easily. Sugar stream stretch readily and molecular chains do not resist the fiber formation like in case of polymers. For that reason, orifice band type spinneret are suitable for sugar processing. Polymer materials need longer melting time and different spinning nozzle geometry which assist the orientation of polymer chains.

Comparison of rotational melt spinning with electrospinning

Rotational melt spinning is compared with electrospinning as nanofiber forming methods. Both spinning techniques have advantages and disadvantages and they are not completely compensatory to each other. Rotational melt spinning is high speed technique when electrospinning is slow method. RMS is one phase method where polymer melting is the most time consuming stage. Spinning of a few grams of polymer takes from 10 to 20 minutes. As for the electrospinning has two phases, the polymer dissolving stage and the spinning stage. The preparation of the solution takes over 24 hours and the spinning process takes from 1 to 3 hours to spin non-woven mat of approximately 5 cm by 5 cm. The longest processing time result to formation of dense mat with grammage of nearly 60 g/m^2. Other mats have grammages between 2-4 g/m^2.

Electrospinning has to be done in fume chamber due to evaporating solvents but rotational melt spinning can be done in room conditions. However an enclosed space would ease controlling of the process. Material properties affect end-products as well as succeeding of spinning processes. Electrospinning processes has no remarkable differences between PLDLA 70/30 and PLGA 80/20 which both are semi-crystalline. However spinning of amorphous PDLA 50/50 do not succeed. It seems that some degree of crystallinity is needed from electrospinnable polymers but also higher iv-values than rotational melt spinnable polymers. Electrospun polymers have iv-values of 3.1 dl/g and 5.72 dl/g when desired iv-values for RMS are in grade of one. However electrospinning result in general to fibers with diameters under 1 μm when rotational melt spinning result to fiber in range of 5-15 μm. This is partly due to the viscosity of molten polymer is higher than the viscosity of solution. Solution properties seems to determine diameters of electrospun fibers due to the needle size, regulated voltage and collector distance do not affect fiber diameters. In rotational melt spinning, the spinning device and material properties both show to have influence in forming fibers.

All electrospun products look like similar non-woven mats when rotational melt spun products have great fluctuation depending on the material. Rotational melt spun products vary from separate fibers or fibrous floss to coarse non-woven mats. As for electrospun products are more dense and thinner mats which are not able to fabricate by RMS. But then sample sizes of electrospun products are smaller. When comparing processing of quite similar polymers PLDLA 96/4 and PLDLA 70/30 with these two methods, it is shown that electrospinning result to round shape fibers with five or more times smaller diameters. Less beads are formed and the end-product is smooth and dense mat when observing without any magnification tools. Rotational melt spun products contain more beads and depending on the nozzle geometry different amount of flat fibers and roughness. Both spinning processes has challenges and beads and fiber cracks are formed in spite of the spinning technique. As a summary, according to this study it seems that these two methods leads to different end-products and they do not exclude each other and both manufacturing methods has suitable applications.

4.3 End products and applications

End-product processed by rotational melt spinning are arbitrary fibrous floss or non-woven webs. Lack of reproducibility exist with the current rms-device and products can not be determined beforehands. End-products are tried to be influenced by decreasing fiber diameters and by different collecting methods. However the direction of fibers into predetermined shape and form is difficult. At the moment the quality of end-product is not sufficient that the fibrous material can be used in any application.

RMS-method is still potential to fabricating fibrous material with varying sized fibers. Light weight and spacious end-products with large surface area are able to be produced. However post-processing of the product would be necessary before final applications. Pore features, the size and the geometry can be partly affected by the shaping and the post-processing. E.g. fibrous material enables compaction of the structure by compression or by needle punching. Thin or thick structures can be produced with different porosity degrees when fiber diameters affect the pore size and geometry. Fibrous floss or fiber webs can be combined with other materials like other textile structures or gels. Fibrous floss could be as space filler or it can be used for modification of surface structure, e.g. by coating other woven or knitted structure. Also fabrication of smoother surface to rougher non-woven structure is able to be carried out.

Nanofibrous materials are interesting alternatives in biomedical field due to high surface area to volume, low mass, small pore sizes but also due to the fiber diameter scale is in the same magnitude with fibrils of extracellular matrix [7]. Then nanofibrous material mimic natural tissue environment and act as cell growth promoting substrate [7]. Rotational melt spun fibrous material contain thicker and thinner fibers. Thinner fibers can be in scale of nanofibers and can promote cell attachment and cell proliferation. Thicker fibers are in scale of microfibers and they can reinforce the structure. Porosity, pore geometry and distribution of open porosities are important features of scaffold structure. Pore structure can determines intercellular contacts and ordering of cells [57]. Cell seeding tensity can be determined by high porosity and high interconnectivity between pores [42]. Rotational melt spun products can produce with variable porosities depending on the fiber collection method and post-processings. By altering the porosity, the capability of material to absorb other substances can be varied. The scaffold structure is then able to manufacture suitable for the desired target tissue. Usually electrospun products have small pore size which inhibit the cellular infiltration migration [7]. As for the pore size of rotational melt spun products is bigger due to larger fiber diameters and the structure is more suitable for cell infiltration.

Biodegradable nanofiber assemblies are reported to be used in formation of capillaries of microvascular system. In those cases fiber assemblies are mold into a composite structure and after the molding fibers are dissolved [5]. The remain structure do not contain nanofibers anymore but microchannel network with similar structure to dissolved fibers exist [5]. Rotational melt spun fibrous structure could be used in this kind of cell growth guiding applications. Fibrous structure without dissolving the fibers may also guide cell growth. This can be exploited e.g. when fibers are combined with hydrogels or some other composite matrix. The cell growth promoting feature would be exploited to provide vascularization. Properties of the composite can be affected by altering the degradation rates of matrix and fibers. Fibers can be impregnated into fast degradation rate material or into slowly degradable material.

Other wide application area in biomedical field is wound care. Nanofibrous products are used as wound dressings due to they are not causing high surface pressures locally but the pressure is spread evenly [34]. Nanofibrous assemblies can also be used in treatment of refractory wounds, for example caused by diabetes or aging diseases. Cotton candy like glass fiber floss with fiber diameter range from 300 nm to 5μm is reported to be used in treatment of this kind of wounds [60]. The wound is filled with the fibrous material and the material is reported to mimic the microstucture of naturally occurring fibrin clot and assist the wound recovery. Normal scarring did not occurred. [60] Rotational melt spun products have great potential in these kind of wound care applications. Soft feeling and material formability ease the usage.

5. SUMMARY

Rotational melt spinning is studied as a fabrication method of micron and sub-micron sized fibers. The method is evaluated as a potential alternative to electrospinning which is a common nanofiber manufacturing method. The research study is done using commercial table sized device which is originally designed for sugar processing. Small modifications to the device are done to make it more suitable for processing of polymers. The effect of different processing parameters are studied and critical parameters are determined. Still further optimization of the device and the process is required to result usable and repeatable processes.

Rotational melt spinning studies are done with constant rotation speed of 2800 rpm. The effect of spinneret design is studied using three different spinnerets. Heating variations are studied by altering heating functions in relation to time and a start-up of rotation. Heating processes are not accurate and temperature measurements are only suggestive. Different collector bowls are used for evaluation of the effect of cooling process to end-products. Effect of material properties are evaluated by processing four different polymers, PLDLA 96/4, PDLA 50/50, PLCL 70/30 and PCL. Results are joint effects of material properties, design of the device and variation of processing parameters where design of the device and material properties seems to be most crucial parameters. In this study the design of the device is the most limiting factor. Rotation speed determines the strength of fiber forming force and the existing device has unchangeable and relatively slow rotation speed compared to literature values. Rotation speed posses weak driving force to fiber formation.

Still different end-products are able to manufacture with the existing device. Separate fibers, fibrous floss and non-woven web with fiber diameters varying generally between 5-15 μm are formed. Each sample has fluctuation in fiber diameters but on average fiber diameters are large compared to sub-micron sized target values. Fibrous floss is formed when fibers are solidified fast after formation and they do not glue together. Polymers with higher glass transition temperature like PLDLA 96/4 and PLDLA 50/50 are transformed into floss structure. Low glass transition temperature polymers PCL and PLCL 70/30 form non-woven web structure when fibers are glued together before solidification. Plastic PLDLA 96/4 with the highest crystallinity degree result to the smoothest fibers with most even fiber diameter distribution. As for semi-crystalline but elastic PCL do not stretch sufficiently and fluctuation of fiber diameters is high. Also huge amount of beads are formed. Fibers and the fibrous material contain relatively huge number of faults and roughness, like beads, needles and fiber breakages. Transverse cracks and lines on the surface of fibers are found. Surface faults are most probably caused by high viscosity of material and the nozzle geometry but reason for faults are not been able to explain more carefully. Round shape spinning nozzle result to smoother and more homogenous fibers with less roughness than the spinneret with narrow cavity opening, although smaller fiber diameters are able to achieve with narrow cavity spinneret. It seems that the round shape nozzle is more suitable for fabrication of polymeric fibers but the diameter of the opening is too large. In general the quality of end-products and controlling of the process needs further optimization and upgrading.

In future a few upgrades for the device should be done as measures to improve rotational melt spinning process. The rotation speed should be increased at least up to 5000–6000 rpm but the increase would be higher as well. A voltage regulated heating system is only suggestive at the moment and in future a thermoelement should be integrated into a spinning device to ensure more accurate temperature adjustment and measurement. A tapering furrow spinneret result to better quality end-products and for that reason a round shape opening would be a good alternative to nozzle geometry. However the diameter of 0.5 mm seems to be too large and the diameter of 0.1 mm or less would be more suitable. As an improvement the opening hole would be got smaller and at the same time the number of spinning nozzles would be reduce from four to two. As a final improvement the outer geometry of the spinneret would be designed to enhance fiber stretching, e.g. by adding a perforated plate on the spinneret.

In summary the rotational melt spinning technique is potential but the existing machine is small scale device which is not sufficient for processing of polymers. It is also shown that rotational melt spinning and electrospinning are not exclusive fiber spinning methods. Electrospinning result to thinner fibers, generally less than 1 μm when rotational melt spinning result to microscale fibers. Electrospun products are usually dense non-woven mats. Rotational melt spinning result more often separate fibers and lower density of the end-product. As an advantage of rotational melt spinning method, no harmful solvents are used and fiber formation rate is high. But then the fiber diameter distribution is wider. In conclusion, this work is a basic study of rotational melt spinning method and critical parameters are determined. However the existing device is not suitable for processing of polymers or at least great upgrades are needed. Results of this study can be used as a basic data in development of the rotational melt spinning technique and a new fiber spinning device.

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