PRODUCTION OF ULTRA-THIN NANOFIBERS BY ELECTROSPINNING AND FILTRATION EFFICIENCY TESTS

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Electronic and Land Planning Engineering
Major in Environmental Remediation Technologies

Master of Civil, Environmental and Land Management Engineering

Production of ultra-thin nanofibers by electrospinning and filtration efficiency tests

by Francesca Camilla Bruno

Electrospinning is a straightforward process that uses an electric field to produce polymer ultrathin nanofibers in the range of 100 nm by creation and elongation of an electrified driven jet of polymer solution. This method produces fibers with different sizes and shapes, among which beads, spider webs, branches, flat ribbons, and split longitudinally fibers.

The first aim of this study was to understand the electrospinning process at a scientific level in order to correlate the effects of the operational parameters on the nanofibers structure. Solutions properties such as concentration and age, operational and ambient parameters such as distance tip-to-collector and humidity are the key factors that influence the nanofibers structure.

The second aim of the study was to verify if and how the fibers influence the efficiency of a commercial filter when sprayed on its surface. The filtration tests were performed in different set-up conditions, analyzing the efficiencies of different types of filters with and without nanofibers on them. Different kinds of nanofibers structures split on filters surfaces produced with different polymer solutions were tested.

It has been found that ultrathin nanofibers strongly improve the efficiency of a commercial filter if split on its surface. An increase of the efficiency and pressure drop has been recorded with nanofibers created with high viscosity of the solution, long collecting time, short distance tip-to-collector and tested with low face velocity.
L'electrospinning è un processo che utilizza un campo elettrico al fine di generare nanofibre ultrafini aventi un diametro medio di 100 nm. Le fibre sono create attraverso l'elongazione di un jet elettrificato ricavato da una soluzione di polimeri. Tale metodo produce fibre con differenti diametri e forme, tra cui sfere, ragnatele, diramazioni, nastri e fibre scisse longitudinalmente.

Il primo obiettivo della ricerca riguarda lo studio dettagliato del processo dell'electrospinning, col fine di correlare gli effetti dei parametri operativi sulla forma delle nanofibre. Le proprietà quali concentrazione ed età della soluzione, parametri operativi e ambientali come la distanza tra il punto di espulsione della soluzione e la superficie piana e l'umidità sono i fattori chiave che determinano la morfologia delle nanofibre.

Il secondo obiettivo della ricerca è verificare se e come le fibre influenzano l'efficienza di filtrazione di un filtro in commercio qualora posizionate sulla superficie. L'analisi è stata eseguita attraverso esperimenti di filtrazione con diversi set-up operativi, attraverso cui è stata valutata l'efficienza di diverse tipologie di filtri, con presenza e assenza di nanofibre sulla superficie. Le analisi sono state svolte con nanofibre create con differenti soluzioni e con diversa morfologia.

Da questo studio emerge che le nanofibre ultrasottili, quando posizionate sulla superficie di un filtro in commercio, ne migliorano notevolmente l'efficienza. È stato registrato un aumento di efficienza e di perdita di carico in esperimenti effettuati con ridotta velocità tangenziale su filtri aventi nanofibre create da soluzioni con alta viscosità, limitato tempo di deposito e breve distanza tra il punto di espulsione della soluzione e la superficie piana.
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Chapter 1

Introduction

1.1 Objectives and Approach

The aim of this study was to analyse the behaviour of ultrathin nanofibers made by electrospinning. Two parallel approaches were kept: (1) understand the electrospinning method at a scientific level in order to correlate the effects of the changing parameters of the production on the nanofibers structure, (2) verify if and how the fibers influence the efficiency of a commercial filter when sprayed on its surface. In this thesis the electrospinning method was utilized in the preparation of nanofibers made from a Nylon-6 over formic acid solution. Many properties and different shapes of electrospun fibers were examined for their suitability for use in filtration applications. The filtration tests were performed in different set-up conditions, analysing the efficiencies of different types of filters with and without nanofibers on them. Different kinds of nanofibers structures split on filters surfaces produced with different polymer solutions were tested.

1.2 Electrospinning

Ultrathin nanofibers are a unique nanomaterial because of the scaled dimensions in the cross-sectional direction and the macroscopic length of the fiber axis. Therefore, nanofibers have both the advantages of functionality due to their nanoscaled structure and the ease of manipulation due to their macroscopic length. In addition, three-dimensional nanofiber network assemblies (nanofibrous membranes or fabrics) provide good mechanical properties and good handling characteristics.

Electrospinning is a versatile method based on an electrohydrodynamic process for forming continuous thin fibers ranging from several nanometers to tens of micrometers and can be used for the one-step forming of thin fibrous membranes. The variety of materials, such as the polymer-solvent systems and polymerless sol-gel systems can be electrospun.
Electrospun nanofibrous membranes with high surface areas have drawn significant attention for their practical applications, such as high-performance filter media, protective clothes, composites, drug delivery systems, scaffolds for tissue engineering, sensors, and electronic devices. The functionalities of the nanofibers or nanofibrous membranes are based on their nanoscaled-size, high specific surface area, and high molecular orientation, and they can be controlled by their fiber diameter, surface chemistry and topology, and internal structure of the nanofibers. In addition, processing innovations to improve not only the controlling of morphologies but also the production capacity of electrospun nanofibers and nanofibrous membranes are in progress. [1]

1.2.1 History of electrospinning

Electrospinning has been first studied by John Zeleny in 1914, who published his studies on the behaviour of fluid droplets at the end of metal capillaries in an electric field. His effort began the attempt to mathematically model the behaviour of fluids under electrostatic forces. Further developments toward commercialization were made by Anton Formhals, and described in a sequence of patents from 1934 to 1944 for the fabrication of textile yarns. Electrospinning from a melt rather than a solution was patented by C.L. Norton in 1936 using an air-blast to assist fiber formation. Between 1964 and 1969 Sir Geoffrey Ingram Taylor studied electrically induced jetting from the surface of a viscous liquid, and he produced the theoretical underpinning of electrospinning. Taylor’s work contributed by mathematically modelling the shape of the cone formed by the fluid droplet under the effect of an electric field: he found that the pendant droplet developed into a cone when the surface tension was balanced by electrostatic force and the jets were ejected from the vertices of the cone with diameters significantly smaller then the diameter of the needle when the electrostatic force exceeded its surface tension. This characteristic droplet shape is now known as the Taylor cone.

In the early 1990s nanotechnology began its global rise in several fields of technology, and the research on electrospinning increased after the studies of Reneker, Doshi and Rutledge. Several research groups demonstrated that many organic polymers could be
electrospun into continuous ultrafine fibers or fibrous structures with diameters in the range from several micrometres down to tens of nanometres. Since then, the number of publications and patents about electrospinning in many countries throughout the world has been increasing exponentially every year, and further theoretical developments of the driving mechanisms of the process have been studied.

**Figure 1.2:** Number of publications on Nanofibers and Electrospinning published every year between 1999 and 2012.

Fig. 1.2 Shows the number of publications on nanofibers based research work over years. [2]

**Figure 1.3:** Share of nanofiber-active researchers [2].

Fig. 1.3 Shows the geographical analysis of active researchers in nanofiber field. Asia takes the big lead of about 50% in nanofibers research. Especially the contribution in the last 5 years has been astonishing, due to the higher percentage of government
funding allocation in the area of sustainable energy and environment. China, South Korea, Japan, Singapore and Taiwan represent the most prominent locations in Asia for nanofiber activities. Singapore, Japan and South Korea are very active in exploring nanofibers to improve the performance in energy devices as solar cell or fuel cell electrodes, or fine porous battery separators.

Fig. 1.4 Shows how the number of patents has been increasing, particularly in the last 6 years. The key reasons for increasing trends patents include potential impact of nanofibers, rapid pace of competition and perceived importance by industries.

Reznik et al. described the shape of the Taylor cone and the subsequent ejection of a fluid jet. Hohman et al. investigated the relative growth rates of the numerous proposed instabilities in an electrically forced jet once in flight and endeavours to describe the most important instability of the electrospinning process, the bending (whipping) instability.

Another major theme of the publications is the structural morphology of the electrospun nanofibers and the relationship between the structural features and individual processing parameters. The effects of different variables are determined in general or for different polymers.

At the same time, there is also a considerable interest in the potential applications in biomedical, functional material and devices, energy, electronics, etc. Nanofibers have gained popularity due to their versatility and their properties: high surface area to volume ratio, high porosity, flexibility in surface functionalities and superior mechanical properties. These outstanding qualities make them to be the optimal candidates for a broad range of important applications in widely different areas such as wound dressing, protective clothing, electrodes, sensors, catalysts, drug carriers, tissue scaffolds, battery/cell and capacitor, filters. [4, 9, 10]
1.2.2 Electrospinning process

The process of electrospinning is based on the principle that a strong electrical force overcomes weaker surface tension of a polymer solution at certain threshold to eject a liquid jet. This process could trace its root back to the process of electrospray in which small solid polymer droplets are formed. Both techniques involve the use of a high voltage to initiate and accelerate a liquid jet from the tip of a capillary. The liquid jet in electrospray breaks into small droplets as a result of low viscous solution used, while a solid and continuous fiber is generated in electrospinning as a charged jet composed of a highly viscous polymer solution.

A schematic illustration of the basic setup for electrospinning is shown in Fig. 1.6. A typical electrospinning setup consists of three major components: a high voltage power supplier, a syringe with a metal needle connected to a syringe pump, and a grounded conductive collector.
Chapter 1. Introduction

Figure 1.6: Electrospinning apparatus.[4]

It is possible to simply place the capillary perpendicularly, letting the polymer fluid dropping with help of gravitation and lying on the collector underneath, or tilt the capillary at a defined angle to control the flow, or place it horizontally. The electrode can be inserted either in the polymer fluid or placed onto the tip of the capillary. The collector is usually a plane metal sheet or a grid that can be covered with a fabric.

In the process, a high voltage is applied to a droplet formed from a polymer solution or melt at the tip of the metal needle.

The charges are usually carried by ions, which may move through the fluid faster, commensurate with, or slower than the shape of the fluid changes. For a fixed quantity of fluid, the Coulomb repulsion between the charged ions favours the creation of shapes such as a jet, while the surface tension of the fluid favours sphere-like shapes with smaller surface area per unit mass. As the intensity of the electric field is increased, the hemispherical surface of the fluid at the tip of the capillary tube elongates to form a conical shape known as the Taylor cone (the base region).

Figure 1.7: Photograph of a meniscus of Polyvinyl Alcohol in aqueous solution showing a fibre drawn from a Taylor Cone.[5]
When the electrical potential of the surface is increased to a sufficiently high value, the electrical forces act in opposition to, and dominate the surface tension of the fluid. A charged jet of fluid is then ejected from the apex of the cone.

Although the setup for electrospinning is extremely simple, the detailed experimental and theoretical analysis reveals that the electrospinning process is highly complex since it is controlled by various types of instabilities such as the Rayleigh instability, an axisymmetric instability, and whipping or bending instability. The last one, which is mainly caused by the electrostatic interactions between the external electric field and the surface charge on the jet, was identified as the one that controls the acceleration, stretching, elongation and thinning of the electrospun nanofibers. The other types of instability give rise to fluctuations of the radius of the jet and may eventually result in droplet formation.

The electrified liquid jet is accelerated towards the grounded collector by the electric field and thins rapidly due to the evaporation of the solvent and elongation by stretching and whipping. The path of the jet is from a liquid surface that is through a straight segment of a tapering cone, then through a series of successively smaller electrically driven bending coils and finally solidifying into a continuous thin fiber randomly oriented.

In the straight segment, the flow direction (the trajectory of a segment of the jet) was parallel to the axis of the jet, and along the instantaneous path of the jet. The bending perturbations began and then grew rapidly into a coil, under the influence of the charge carried with the jet. The growing perturbed path of the charged jet was quickly bent into a three-dimensional coil, which was carried downstream and increased in diameter as both the elongation and the bending continued. Typically, the electrical bending coil began at a particular distance from the orifice, and the diameter of the turns of the coil grew larger and moved toward the collector. The elongation rate of the jet was so high that if the jet did not coil, much kinetic energy would be required to keep the leading part ahead of the following parts of the jet. By coiling, the electrical energy supplied to the jet was instead used efficiently to elongate the jet, decrease its diameter, and thereby produce more surface area per unit mass of fluid. The elongation of each segment by the electrical forces caused by the charge carried with the jet continued. As the diameter of the jet decreased the path of the jet again became unstable and a new, smaller diameter electrical bending instability developed. A succession of three or more smaller diameter bending instabilities was often observed before the jet solidified. As a result, such jets acquired fractal-like configurations, and their length increased enormously as their cross sectional diameter decreased to a fraction of a micron.
The morphology and diameter of electrospun fibers depend on a wide range of processing parameters. These parameters are classified into three major categories which are solution properties, controlled variables, and ambient parameters.

- Solution properties include the type, the conformation, the dipole moment, the dielectric constant, crystallinity, glass transition temperature, molecular weight, and molecular weight distribution of the polymer; the vapor pressure, the polarity, and surface tension of the solvent; viscosity/concentration, elasticity, electrical conductivity; age of the solution. The effects of the solution properties are difficult to be isolated since varying one parameter may affect other solution properties.

- Controlled variables include the solution feeding rate, electric field strength, distance between the tip and the collector, needle diameter, shape and length, composition, geometry and motion of the collector.

- Ambient parameters include temperature, humidity, air velocity.
By tuning the above parameters, it is possible to obtain nanofibers in a controlled way. [9]

Besides circular fibers, a variety of cross-sectional shapes and sizes can be obtained from different polymer solutions during the process: branched fibers, flat ribbons, bent ribbons, ribbons with other shapes, spider webs, droplets, beaded fibers, and fibers that were split longitudinally from larger fibers.

Studies on the properties of fibers with these cross-sectional shapes from a number of different kinds of polymers and solvents indicate that fluid mechanical effects, electrical charge carried with the jet and evaporation of the solvent all contributed to the formation and shape of the fibers. The concentration, the molecular weight and the viscosity form a trinity of parameters, all affecting the fiber forming ability of the solution, also termed electrospinnability. In particular, the viscosity, which measures the resistance of the fluid to flow and influences proportionally its surface tension, plays an important role, since it stabilizes the jet. [11]

For a fixed quantity of fluid, the Coulomb repulsion between the charged ions favours the creation of shapes such as a jet, while the surface tension of the fluid favours sphere-like shapes with smaller surface area per unit mass as a result of the longitudinal Rayleigh instability. When the electrical potential of the surface is increased to a sufficiently high value, the electrical forces act in opposition to, and dominate the surface tension of the fluid. A charged jet of fluid is then ejected.

Viscosity is directly proportional to the concentration of the solution and to the molecular weight of the polymer. [12]

### 1.3 Air filtration

The capture of aerosol by filtration is the most common method of aerosol sampling and is widely used for air cleaning. Filtration is simple, versatile, and economical means for achieving high-efficiency collection of submicrometer particles.

The filtration of nanoparticles is becoming an important issue as they are produced in a greater and greater number of nanotechnology means, material synthesis and combustion emissions. They may pose a risk for the environment and human beings because nanoparticles could in their life-time enter our atmosphere, soil or water environments. The risk of these entering the environments, as well as the effects on human health,
is increasing because they can readily enter the human body through inhalation and absorption and their toxicity is relatively high due to the large specific surface area. [13] Inhalation can occur at home, in the workplace, and in the ambient environment. Epidemiological studies have found a higher incidence of chronic obstructive pulmonary disease, fibrosis, and lung cancer in workers exposed to certain types of nanoscale particles. There is an increasing body of scientific literature on the adverse health effects of inhaled nanoscale particles, but the dosimetry and toxicology are still not well understood. Aerosol filtration is used in diverse applications, such as respiratory protection, air cleaning of smelter effluent, processing of hazardous material, and clean rooms.

The process of filtration is complicated, and although the general principles are well known there is still a gap between theory and experiment. Nevertheless, filtration is an active area for theoretical and experiment research, and there is an extensive scientific literature on the subject.

### 1.3.1 Fibrous filters

Fibrous filters are simple and economical devices capable of efficiently removing submicrometer particles from gas streams. They consist of a mat of fine fibers arranged in a way that most are perpendicular to the direction of airflow. These filters have a porosity from 70% greater than 99%, with fiber range in size from tens of nanometer up to 100 micrometer. Particles are removed by a fibrous filter when they collide and attach to the surface of the fibers. Because fibers can be made of a wide variety of materials, such as cellulose, glass, plastics, ceramics, or metals, fibrous filters have been applied in many areas, including disposable respirators, industrial gas cleaning equipment, cleanroom air purification systems, automotive cabin air filters, and indoor air purifiers. They have also been employed to collect samples of aerosol particles for chemical analysis. [14]

Collection efficiency and pressure drop are the parameters used to assess the performance of a filter. A good filter should have high collection efficiency and low pressure drop. At a given rate of aerosol flow, the collection efficiency is a function of particle size. The most penetrating particle size, defined as the particle size for which a filter has the lowest collection efficiency, has also been adopted as a performance indicator. The collection efficiency is defined as the fraction of the entering particles that are collected by the filter, expressed either in terms of particle collection efficiency $E$ or a mass collection efficiency $E_m$:

$$
E = \frac{N_{in} - N_{out}}{N_{in}} \quad (1.1)
$$

$$
E_m = \frac{C_{in} - C_{out}}{C_{in}} \quad (1.2)
$$

where $N$ and $C$ refer to the number and mass concentration, respectively, of particles entering and leaving the filter.

Filters are usually characterized in terms of penetration $P$: fraction of entering particles that penetrate the filter. For a high-efficiency filter, the penetration is a clearer indicator
because it is a smaller number and therefore shows a larger relative change than does the collection efficiency. For instance, when $E$ increases from 90 to 99%, $P$ drops from 10 to 1%.

$$P = \frac{N_{out}}{N_{in}} = 1 - E$$  \hspace{1cm} (1.3)$$

$$P_m = \frac{C_{out}}{C_{in}} = 1 - E_m$$ \hspace{1cm} (1.4)$$

The flow velocity at the face of the filter is called *face velocity*, $U_0$:

$$U_0 = \frac{Q}{A}$$ \hspace{1cm} (1.5)$$

where $Q$ is the volumetric flow rate through the filter and $A$ is the cross sectional area of the filter exposed to the entering airstream.

Inside a filter, the air velocity $U$ is slightly greater than $U_0$, because the the volume for the air passage is reduced by the volume of fibers:

$$U = \frac{Q}{A(1 - \alpha)}$$ \hspace{1cm} (1.6)$$

where $\alpha$ is the volume fraction of fibers in a filter, known as the *packing density* or *solidity*. It is an important parameter influencing the filter performance. Commercial fibrous filters typically have values between 0.01 and 0.3.

$$\alpha = \frac{\pi d_f^2}{4hd_f} = \frac{\text{fiber volume}}{\text{total volume}} = 1 - \text{porosity}$$ \hspace{1cm} (1.7)$$

Fibrous filters can be thought of as many thin layers of filters, each having a certain probability of collecting particles of given size. Thus, the filtration efficiency for monodisperse aerosols increases as the thickness of a filter is increased.

If $\gamma$ represents the fractional capture per unit thickness for a differentially thin layer $dt$, then the number of particles captured $n_c$ when a unit volume of aerosol passes through a layer is

$$n_c = N\gamma dt$$ \hspace{1cm} (1.8)$$

where $N$ is the particle number concentration entering the layer. The decrease in concentration of an aerosol passing through the layer is equal to $n_c$. the number of particles captured per unit volume of aerosol passing through the layer; that is

$$dN = -n_c = -N\gamma dt$$ \hspace{1cm} (1.9)$$

The combined effect of all the layers is obtained by integrating $1.9$ over the entire thickness $t$:
\[
\int_{N_{in}}^{N_{out}} \frac{dN}{N} = \int_0^t (-\gamma)dt
\]

(1.10)

to get

\[
ln \frac{N_{out}}{N_{in}} = -\gamma t
\]

(1.11)

\[
P = e^{-\gamma t}
\]

(1.12)

Thus, particle penetration decreases exponentially with increasing filter thickness.

The structure of a filter creates a resistance to the air flowing through it, called the pressure drop, \(\Delta p\). At a given face velocity, the pressure drop of a filter is directly proportional to the thickness of the filter. Since the flow inside most filters is laminar, the pressure drop is directly proportional to the flow rate. A change in any property of a filter, such as its fiber or pore size, \(\alpha, \gamma, U_0\), or \(t\) causes a change in both the efficiency for a given particle size and the pressure drop. The best filter is the one that gives the highest collection efficiency with the least pressure drop.

In fibrous filters, both efficiency and pressure drop increase with dust loading, the accumulation of collected particles in the filter. Initially this is beneficial, but eventually, the pressure drop becomes excessive and the filter is said to be clogged.

### 1.3.2 Single Fiber Efficiency

Fibrous filtration is a complex process, and only by analysing this process at its most elementary level, the collection of a particle by an individual fiber, does the influence of various parameters become apparent.

The approach is to consider a single fiber, positioned with its axis perpendicular to the airflow in the middle of a filter, and analyse the several mechanism by which particles can be collected on that fiber. It is assumed that a particle sticks if it contacts the fiber and is permanently removed from the aerosol stream.

An examination of the Reynolds number \(Re_f\) that characterises the flow around a fiber having a diameter \(d_f\) reveals that, under most conditions, the flow inside a filter will be laminar.

\[
Re_f = \frac{\rho_d d_f U}{\eta}
\]

(1.13)

The efficiency with which a fiber removes particles from an aerosol stream is defined in terms of a single fiber efficiency \(E_{\Sigma}\), a dimensionless particle deposition rate on a unit length of fiber. \(E_{\Sigma}\) is the ratio of the number of particles collected by a fiber in one second to the number that would have passed through an imaginary outline of the fiber in one second.

\[
E_{\Sigma} = \frac{\text{number collected on unit length}}{\text{number geometrically incident on unit length}}
\]

(1.14)
The overall efficiency of a filter \( E \) is a function of \( E_\Sigma \). Assuming that all fibers in a filter have the same diameter, the total length \( L \) of fiber in a unit volume can be obtained from \( \alpha \):

\[
L = \frac{4\alpha}{\pi d_f^2}
\]  

(1.15)

From the definition of \( E_\Sigma \), the number of particles collected when a unit volume of aerosol passes through an element of unit cross sectional area anf thickness \( dt \) is

\[
n_c = NE_\Sigma d_f L dt
\]  

(1.16)

1.16 is the same of 1.8 with

\[
\gamma = E_\Sigma d_f L
\]  

(1.17)

Combining 1.15 and 1.17 gives

\[
\gamma = \frac{4\alpha E_\Sigma}{\pi d_f}
\]  

(1.18)

thus 1.11 becomes

\[
P = 1 - E = e^{-\gamma t} = e^{\frac{-4\alpha E_\Sigma t}{\pi d_f (1-\alpha)}}
\]  

(1.19)

1.19 relates the macroscopic property of filter penetration to the microscopic property of a single fiber efficiency \( E_\Sigma \).

### 1.3.3 Deposition mechanisms

As an aerosol stream approaches a fiber, particles may deposit on the fiber by the simultaneous action of several mechanisms, including:

- Inertial impaction
- Interception
- Diffusion (Brownian motion)
- Gravitational settling
- Electrostatic deposition

The first four mechanisms do not depend on electrostatic forces and are known as mechanical capture mechanisms.

To calculate the overall collection efficiency due to all mechanisms acting together, it is
usually assumed that the efficiencies due to individual mechanisms are additive. Such an approach tends to overestimate the overall efficiency, because the capture of a particle could be counted more than once. For the particle size range in which one capture mechanism predominates, it has been shown that the efficiency due to that mechanism alone gives a better estimate of the overall efficiency than does the sum of all individual mechanism efficiencies. [15]

**Interception** takes place because a particle has a finite size, which leads to deposition when it comes within one particle radius of the fiber surface, even though it stays on the original streamline.

![Figure 1.9: Single-fiber collection by interception.](image)

For pure interception, it is assumed that the particles follow the streamlines perfectly. This is the only mechanism that is not a result of a particle departing from its original gas streamline, and so it does not depend on flow velocity $U_0$.

The single-fiber efficiency due to interception depends on the dimensionless parameter $R$, where

$$R = \frac{d_p}{d_f}$$  \hspace{1cm} (1.20)

For $R < 0.2$ and $\alpha < 0.5$, the single fiber efficiency due to interception $E_R$ can be calculated from the following expression:

$$E_R = \frac{(1 + R)^{(-1)} - (1 + R) + 2(1 + 1.996 \, Kn)(1 + R) \ln(1 + R)}{2(-0.75 - 0.5 \, ln\alpha) + 1.996 \, Kn(-0.5 - ln\alpha)}$$  \hspace{1cm} (1.21)

where $Kn$ the Knudsen number. The Knudsen number indicates that molecular effects of gas are important and is $Kn = 2\alpha/d_f = 0.88$ under standard conditions.

From 1.21 follows that a finer fiber is more efficient than a coarser fiber in intercepting particles. $E_R$ increases with increasing $R$, but cannot exceed the maximum theoretical value of $1 + R$ based on the definition of single-fiber efficiency.
The pressure drop based on the Kuwabara flow with slip effect is:

\[
\Delta p = \frac{4 \mu t U_f (1 + 1.996 Kn)}{0.25 d_f^2 [-0.5ln\alpha - 0.75 + \alpha - \alpha^2/4 + 1.996 Kn (-0.5ln\alpha - 0.25 + \alpha^2/4)]}
\]

(1.22)

where \(\mu\) is the air viscosity, \(U_f\) the face velocity and \(Kn\) is the Kuwabara hydrodynamic factor, a dimensionless factor that compensates for the effect of distortion of the flow field around a fiber because of its proximity to other fibers. \(Kn\) depends only on the solidity \(\alpha\):

\[
Kn = \frac{-ln\alpha}{2} - \frac{3}{4} + \alpha - \frac{\alpha^2}{4}
\]

(1.23)

for \(\alpha = 0.005\). For \(\alpha = 0.2\), \(Kn = 0.25\).

**Inertial impaction** occurs when a particle, by its inertia, is unable to adjust quickly enough to the abruptly changing streamlines and hits a fiber.

![Figure 1.10: Single-fiber collection by inertial impaction.](image)

Inertial impaction of a particle is related to the flow field around the particle, which is characterized in terms of the particle Reynolds number. For \(Re < 1\), the governing parameter for inertial impaction is the Stokes number \(Stk\):

\[
Stk = \frac{\tau U_0}{d_f} = \frac{\rho_p d_f^2 C_c U_0}{18 \eta d_f}
\]

(1.24)

where \(\rho_p\) is the particle density, \(C_c\) is the slip correction factor, \(\eta\) is the viscosity of the gas. This equation represents the ratio of the persistence of a particle to the size of the target. Single-fiber efficiency for impaction increases with an increasing value of Stokes number: greater particle inertia (greater \(d_p\) or \(\rho_p\), greater particle velocity, or more abrupt curvature of streamlines, caused by smaller fiber size.

The slip correction factor \(C_c\), a correction to the Stokes friction coefficient for particles having a size comparable with or smaller than the mean free path of the gas molecules \(\lambda\), can be evaluated from the following empirical equation:
\[ C_c = 1 + \frac{2 \lambda}{d_p} (1.165 + 0.483 e^{-0.997 \frac{d_p}{\pi}}) \]  

(1.25)

For small Stokes number, the following equation can be used to calculate the single fiber efficiency \( E_I \) due to inertial impaction:

\[ E_I = \frac{Stk^3}{Stk^3 + 0.77Stk^2 + 0.22} \]  

or with:

\[ E_I = \frac{Stk \cdot J}{2 Ku^2} \]  

(1.27)

where

\[ J = (29.6 - 28 \alpha^{0.62})R^2 - 27.5R^{2.8} \]  

(1.28)

The equation is valid for \( 0.01 < R < 0.4 \) and \( 0.0035 < \alpha < 0.111 \). There is not simple equation for \( J \) when \( R > 0.4 \), for approximate analysis, a value of \( J = 2.0 \) for \( R > 0.4 \) can be used.

Interception and inertial impaction are the most important mechanism for large particles, and the sum of \( E_R \) and \( E_I \) cannot exceed the theoretical maximum of \( 1 + R \).

For particles smaller than a few tenths of a micrometer, the Diffusion (Brownian motion) can be sufficiently strong to move them from the original streamlines to a fiber.

![Figure 1.11: Single-fiber collection by diffusion.](image)

The governing parameter for convective Brownian diffusion is the Peclet number \( Pe \), that determines the single fiber efficiency \( E_D \) due to diffusion.

\[ Pe = \frac{d_f U_0}{D} \]  

(1.29)

where \( D \) is the particle diffusion coefficient:

\[ D = \frac{0.0000000000000000138 C_c 293}{3 \pi d_p \eta} \]  

(1.30)
Chapter 1. Introduction

The equation of efficiency $E_D$ is based on experimental measurements:

$$E_D = 2.27K_u^{(-1/3)} Pe^{(-2/3)} (1 + 0.62 \frac{2\gamma}{d_f} Pe^{(1/3)} K_u^{(-1/3)}) \quad (1.31)$$

Single-fiber efficiency increases as $Pe$ and particle size decrease. $E_D$ is the only mechanism that increases as $d_p$ decreases.

In estimating the overall single-fiber collection efficiency near the size of minimum efficiency, it is necessary to include an interaction term to account for enhanced collection due to interception of the diffusing particles:

$$E_{DR} = 1.24 \frac{R^{2/3}}{(Ku Pe)^{1/2}} \quad (1.32)$$

for $Pe > 100$.

**Gravitational settling** can contribute to particle collection if the aerosol stream flows downward, but the contribution is negligible for nanoparticles.

Electrostatic forces (**Electrostatic deposition**) arise when particles or fibers carry electric charges or when an external electric field is applied to the filter. There are several types of electrostatic interactions: among them is the *Coulombic attraction* between a charged particle and an unipolar or bipolar charged fiber. Secondly, an unipolar or bipolar charged fiber can polarize a neutral particle, thereby giving rise to *dielectrophoretic forces* (or *dipole*) on the particle. An externally applied electric field can polarize a fiber and the nonuniform field thus created around the fiber can move a charged particle toward the fiber. Polarization of particles by an externally applied electric field also can produce dielectrophoretic forces on them. Another type of electrostatic interaction is the *image force* between a charged particle and a neutral fiber, as a result of polarization of the fiber by the particle charge. Image forces are weaker than Coulombic forces.

![Figure 1.12: Different kinds of electrostatic interactions.](image)
This mechanism is difficult to quantify because it requires knowing the charge on the particles or on the fibers. It is often neglected, unless the particles or fibers have been charged in some quantifiable way. Increasing the charges or reducing the face velocity increases the collection efficiency.

1.3.4 Filter efficiency

The overall efficiency of a filter can be determined by 1.19 if the total single-fiber efficiency $E_{\Sigma}$ is known. The mechanical single-fiber efficiencies are correctly summed as long as each acts independently and is less than 1.

$$E_{\Sigma} = E_R + E_I + E_D + E_{DR}$$  \hspace{1cm} (1.33)

1.14 shows the filter efficiency for individual single-fiber mechanism and the total efficiency.

![Figure 1.13: Single-fiber collection by electrostatic forces.](image1.png)

**Figure 1.13:** Single-fiber collection by electrostatic forces.

![Figure 1.14: Filter efficiency for individual single-fiber mechanism and the total efficiency for a filter with $t = 1mm$, $\alpha = 0.05$, $d_f = 2\mu m$, and $U_0 = 10cm/s$.](image2.png)

**Figure 1.14:** Filter efficiency for individual single-fiber mechanism and the total efficiency for a filter with $t = 1mm$, $\alpha = 0.05$, $d_f = 2\mu m$, and $U_0 = 10cm/s$. 
Since these mechanisms are competing each other, for a given fibrous filter there is particle size, usually between 0.05 and 0.5 \( \mu m \), that has the minimum collection efficiency. All particles, larger or smaller than this size, are collected with a greater efficiency. For a given size particle, there is also a velocity for minimum collection efficiency. [14]

\[ \text{Figure 1.15: Filter efficiency versus particle size for face velocity of 1 and 10 cm/s, with } t = 1mm, \alpha = 0.05, d_f = 2\mu m. \]

The total penetration for one filter with \( t \) thickness is calculated with 1.19.
Chapter 2

Materials and Methods

2.1 Electrospinning

The electrospinning experiments have been developed inside of a closed grounded chamber. The capillary has been maintained horizontal and a pump was used to initiate the droplet. The apparatus consisted of a syringe containing polymer solution placed on a syringe pump, with a high voltage power supply connected through a cable on the needle, and a grounded metal collector plate in front of it.

In the next paragraphs every instrument will be explained in details.

2.1.1 The chamber

The whole equipment was placed in a grounded chamber of 100x50x60 cm with walls made of PMMA (Polymethyl methacrylate - acrylyc) and bottom made of PVC (polyvinyl chloride). It had two controllable fans, a precise thermometer and a moisture meter.

Figure 2.1: Experiments have been developed inside a grounded chamber.
2.1.2 Apparatus

Sterile single-use latex free syringes of 5 ml (6 ml) volume (*Henke Sass Wolf*) have been used to contain the polymer solution. Sterile metal needles with different diameters have been utilised and connected with the high voltage power supply: 19x0.4, 25x0.7 and 40x1.2 mm size (*BD Microlance*). The standard diameter was 0.4 mm.

To initiate the polymer solution, the syringes were placed on a syringe pump (*NE-300, New Era Pump Systems*) and the solution were pumped at 5 µl/min.

![Figure 2.2: The syringe pump.](image)

The voltages have been generated by a high voltage power supply and applied on the needle tip (*Gamma Research, model ES30R-5W*), in a range from +5 kV up to +30 kV with a step of 5 kV. The standard voltage was +20 kV.

The collector was a grounded plane metal sheet. During every session, a layer of aluminium foil has been put on the collector, and the fibers have been collected on it. In case a blank commercial filter was used, it was attached on the foil at two extremities with a tape. The tip-to-collector distance was in a range from 5 to 30 cm, with a standard distance of 15 cm.

The samples, once created, were dried leaving them inside the chamber with fans on for one day.

2.1.3 Polymer

Nylon-6 (*Sigma-Aldrich, product of USA*) and formic acid (*Sigma-Aldrich, product of Germany*) were purchased to prepare nanofibers.

Nylon-6:

- linear formula: \([-NH(CH_2)_5CO-\]_n\)
Chapter 2. Materials and Methods

2.2

- chemical formula

\[
\begin{array}{c}
\text{H} \\
\text{N} \\
\text{O}
\end{array}
\]

- particle size of 3 mm in pellets form

Formic Acid:

- linear formula: \textit{HCOOH}
- chemical formula

\[
\begin{array}{c}
\text{H} \\
\text{O}
\end{array}
\]

- density of 1.22 g/ml
- purity of \sim 98%

Six different solutions have been prepared by dissolving 5%, 10%, 15%, 20%, 25% (w/w) of nylon-6 in 10 ml of formic acid (See table below) at room temperature. The dissolution of the polymer was performed by shaking in a sonicator (\textit{Bandelin Sonorex}) for 12 hours.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Name</th>
<th>Concentration</th>
<th>PA (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5%</td>
<td>5%</td>
<td>0.610</td>
</tr>
<tr>
<td>2</td>
<td>10%</td>
<td>10%</td>
<td>1.220</td>
</tr>
<tr>
<td>3</td>
<td>15%</td>
<td>15%</td>
<td>1.830</td>
</tr>
<tr>
<td>4</td>
<td>20% A</td>
<td>20%</td>
<td>2.440</td>
</tr>
<tr>
<td>5</td>
<td>20% B</td>
<td>20%</td>
<td>2.440</td>
</tr>
<tr>
<td>6</td>
<td>25%</td>
<td>25%</td>
<td>3.050</td>
</tr>
</tbody>
</table>

\textbf{Figure 2.3:} Concentration and mass of polyamide-6 in 6 different solutions

\textbf{2.1.4 SEM}

Once the samples were dry, the morphology and diameter of the electrospun nanofibers were observed by using field emission Scanning Electron Micrographs SEM (\textit{Nova Nano SEM 230}). This microscope produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with atoms in the specimen, producing various signals that can be detected and that contain information about the sample’s surface topography and composition. SEM can achieve resolution better than 1 nanometer.
Prior to the measurements the specimens were sputter coated to prevent charging of the SEM electron beam. Sputter coating is a technique that makes a target be bombarded with heavy ionised gas, whom metal atoms deposit onto the any surface within the coating unit including the specimen. A plasma produced platinum coating of about 3.2-3.5 nm was applied to the patches (Bal-tec MED 020).

The software ImageJ® has been used for the evaluation of the fiber diameters and their distributions. Four kinds of fibers have been valued: small, medium and large diameter, and spider webs. The final values were the average of 30-40 values for each type of fiber from different images of the same sample.

### 2.2 Air Filtration

A dry air flow containing NaCl nanoparticles has been used to test the efficiency of the filters. The tests have been developed using a DMA to select the nanoparticles size and a CPC to measure the concentrations before and after the filter.

#### 2.2.1 Apparatus

Fig. 2.4 shows a schematic diagram of the nanoparticle filtration test system, and it consists of a nanoparticle generation system, a DMA for size classification and a CPC, a filter penetration measurement system.
The particles flow passed through silicon carbon embedded tubes, that were connected to the vacuum in the end. In the circuit three measuring devices were used: a laminar flow meter before the DMA and two flow meters before and after the CPC. The laminar flow meter was composed by a pressure meter and by a laminar flow element: a cylindrical metal tube that makes the flow laminar. This device is based on the principle that the flow is linearly proportional to the pressure drop that drives the laminar flow through a tube.
An atomizer aerosol generator (TSI, model 3079) was used to generate NaCl nanoparticles from a solution of deionized water (DI) and NaCl. Five different solutions have been prepared by dissolving 0.5%, 1%, 2%, 5% and 10%(w/w) of NaCl in 60 ml of DI water (See table below) at room temperature. The dissolution of the salt was performed by shaking manually first and then in a sonicator (Bandelin Sonorex) for 1 hour.

<table>
<thead>
<tr>
<th>DI water</th>
<th>NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>ml</td>
<td>%</td>
</tr>
<tr>
<td>60</td>
<td>0.5%</td>
</tr>
<tr>
<td>60</td>
<td>1%</td>
</tr>
<tr>
<td>60</td>
<td>2%</td>
</tr>
<tr>
<td>60</td>
<td>5%</td>
</tr>
<tr>
<td>60</td>
<td>10%</td>
</tr>
</tbody>
</table>

Figure 2.5: Concentration and mass of NaCl in DI water in 5 different solutions

Air was used as a carrier gas. The concentration of particles was controlled by changing the air flow passing through the atomizer, the standard flow was 200 nl/h.

The flow dried in a diffusion dryer fulfilled with silicon gel in pellet form and was regulated with a valve in order to have 174 Pa on the pressure meter (corresponding to an air flow of 1 l/m).

The NaCl particles are then classified by a Differential Mobility Analyser (DMA, TSI, model 3080). This instrument can measure the size distribution and concentration of particles in the size range of 2 nm to 1 µm using differential mobility analysis. This method is based on the physical principle that the ability of a particle to traverse an electric field (electrical mobility) is related to particle size. In a DMA, an electric field is created, and the airborne particles are charged, migrate into a clean sheath air flow and drift in the DMA according to their electrical mobility. Since the particles migrate at different rates, they are spread out through the sheath air. Withdrawing a portion of the sheath air flow separates a narrow range of particle mobilities from the rest of the aerosol. To measure a size distribution, the DMA is scanned over a range of particle mobilities by varying the applied field. [6] The sheath flow used was 6.0 l/m, with a consequent possible range of particle size from 9.87 up to 471 nm.
The particle size was controlled by adjusting the DMA voltage. The fractional penetration through test filters was measured for each mobility particle size from 10 to 450 nm for the glass nanofiber filter and paper filter, from 15 to 150 nm for paper filter and from 15 to 450 nm for polyester filters.

Once classified, the NaCl particles passed through a neutraliser. A second clean air flow of 6.5 l/m is added to the flow coming from the DMA and measured with a flow meter. This let to have a face velocity on the filter of 10 cm/s.

The particles are so diluted, introduced to the test filter and then sent in the vacuum. The number of particles upstream and downstream of the filter were measured by a Condensation Particle Counter (CPC, TSI, model 3775). This instrument detects airborne particles down to 4 nm using a diffusional thermal cooling method to enlarge submicrometer particles to a size that can be easily detected. The particle are first enlarged into droplets in a supersaturated gas. As the condensing fluid, CPC uses ethanol. In order to ensure that all particles experience the highest possible supersaturation which occurs along the centre of the saturator, a sheath flow is used to constrain the particles. Here the inlet flow is split into sample and sheath flows, where the sheath flow is filtered and passes through the saturator wick and the sample flow is then injected into the centre of the laminar sheath flow through a capillary. On exiting the saturator, the saturated air is cooled in the condenser, becoming supersaturated and causing particles above a certain size to grow into drops. These drops are then focused through a nozzle, and pass through the laser beam and counted. The sheath flow used was 0.3 l/m.

**Figure 2.6:** Differential Mobility Analyzer. On the right, a scheme of the operating principle[6]
Chapter 2. *Materials and Methods*

2.2.2 Filters

Six kinds of commercial filters have been tested: glass microfiber filter, paper filter and three polyester filters.

**Glass microfiber binder free filter** (*Whatman, CAT no. 1825-090)*:

- Grade GF/F, circle, 90 mm diameter
- Thickness of 420 \( \mu \)m
- Particle retention in liquid (at 98% of efficiency) of 0.7 \( \mu \)m
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**Figure 2.8:** SEM images at different resolution of a Glass microfiber filter.

**Paper filter** (*Whatman, CAT no. 1001-055*):

- Grade 1, circle, 55 mm diameter
- Thickness of 180 µm
- Particle retention in liquid (at 98% of efficiency) of 11 µm

**Figure 2.9:** SEM images at different resolution of a paper filter.
Polyester filter (fiberweb, Style No. 2275 REEMAY):

- 25 g/m² non-whitened
- Thickness of 150 µm
- Tex test air permability 932 cfm

Figure 2.10: SEM images at different resolution of a Reemay 2275 filter. In the picture on the right it is possible to see few nanofibers splitted on its surface.

Polyester filter (fiberweb, Style No. 2214 REEMAY):

- 46 g/m² non-whitened
- Thickness of 220 µm
- Tex test air permability 516 cfm
Polyester filter (fiberweb, Style No. 2295 REEMAY):

- 100 g/m$^2$ non-whitened
- Thickness of 400 $\mu$m
- Tex test air permability 258 cfm

The filter holder used during the efficiency tests accepted 47 mm diameter discs. A filter cutter ?? of this size has been used in a punch press to cut the filters.

Figure 2.11: The filter cutter.
Chapter 3

Results and discussion

This chapter shows and describes the SEM images of the samples created in different conditions and the results of the filtration tests.

3.1 Electrospinning

The analysis on the influence of the parameters on the fibers structure has been performed maintaining them at the standard values and changing a parameter one at the time. The following shows the results obtained changing concentration of the solution, age of the solution, distance tip-to-collector and voltage, humidity and feeding rate. The standard conditions for the production of the fibers via electrospinning were:

- Polymer concentration: 20% (w/w) Nylon-6 over formic acid
- Voltage: + 20 kV
- Distance tip-to-collector: 15 cm
- Collecting time: 10 minutes
- Needle size: 0.4 x 19 mm
- Feeding rate: 5 µl/min
- Temperature and humidity: ambient

3.1.1 Concentration of the solution

For a fixed quantity of fluid, the Coulomb repulsion favors the creation of shapes such as a jet, while the surface tension of the fluid favors sphere-like shapes with smaller surface area per unit mass. Changing the concentration of Nylon-6 brings to different values of viscosity, and so different surface tensions. Increasing the viscosity favours the formation of smooth fibers. As the viscosity of the solution is raised, the shape of the beads changes from spherical to spindle-like, the beads disappear gradually, the fiber diameter larger. Ribbon shaped fibers and spider webs have been found at high concentration.
values.

The following table shows the diameter of the different fibers measured with *ImageJ*.

![Table showing fiber diameters with different concentrations](image)

**Figure 3.1:** Fibers diameters with different concentrations.
Chapter 3. Results and discussion

Figure 3.2: SEM images of the solutions with different concentrations.
3.1.2 Age of the solution

Samples of 10%, 20% A and 25% solutions at different age have been collected. The results show a decreasing of the fibers diameters and of the amount of spider webs, a disappearance of the ribbons and larger fibers and an increasing of the beaded fibers. Compared to a fresh made solution, Nylon-6 is dissolved better in the formic acid after two months with a consequent decrease of the viscosity and so a change of the surface tension.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solution %</th>
<th>Age days</th>
<th>Small um</th>
<th>Medium um</th>
<th>Large um</th>
<th>Spider um</th>
<th>Flat ribbons</th>
<th>Spider web</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>10%</td>
<td>1</td>
<td>0.026</td>
<td>0.072</td>
<td>0.130</td>
<td>-</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>8</td>
<td>10%</td>
<td>60</td>
<td>0.034</td>
<td>0.058</td>
<td>0.157</td>
<td>-</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>4</td>
<td>20%</td>
<td>1</td>
<td>0.127</td>
<td>0.333</td>
<td>1.122</td>
<td>0.061</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>7</td>
<td>20%</td>
<td>60</td>
<td>0.052</td>
<td>0.133</td>
<td>-</td>
<td>0.019</td>
<td>no</td>
<td>few</td>
</tr>
<tr>
<td>6</td>
<td>25%</td>
<td>1</td>
<td>0.402</td>
<td>0.287</td>
<td>1.404</td>
<td>0.031</td>
<td>big</td>
<td>several</td>
</tr>
<tr>
<td>14</td>
<td>25%</td>
<td>71</td>
<td>0.158</td>
<td>0.198</td>
<td>0.262</td>
<td>0.029</td>
<td>no</td>
<td>yes</td>
</tr>
</tbody>
</table>

*Figure 3.3: Fibers diameters of 10%, 20% A and 25% solutions at different age*
Chapter 3. Results and discussion

(a) 10%, 1 day
(b) 10%, 60 days
(c) 20% A, 1 day
(d) 20% A, 60 days
(e) 25%, 1 day
(f) 25%, 71 days

Figure 3.4: SEM images of 10%, 20% A and 25% solutions at different ages.
3.1.3 Distance tip-to-collector

At short distance, fibers appear slightly larger and with several dense spider webs. The collecting area is smaller and the amount of fibers layers is higher. When the collector is further, the collecting area is larger and includes part of the chamber bottom close to the collector. The number of layers decreases, the spider webs become less dense and gradually disappear. Mean diameter is larger. As shown in 1.8, the path of the jet is through a straight segment, then through a series of successively smaller electrically driven bending coils and finally solidifying into a continuous thin fiber randomly oriented. Moving the collector closer or further from the needle brings to the solidification of different part of the jet. At the maximum distance, the thinner fibers, with less net charge density carried by, do not reach the collector but deposit on the bottom, differently from the larger fibers that solidify on the collector.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solution %</th>
<th>Age days</th>
<th>Distance cm</th>
<th>Small um</th>
<th>Medium um</th>
<th>Large um</th>
<th>Spider um</th>
<th>Flat ribbons</th>
<th>Spider web</th>
</tr>
</thead>
<tbody>
<tr>
<td>27</td>
<td>20% B</td>
<td>23</td>
<td>5</td>
<td>-</td>
<td>0.123</td>
<td>-</td>
<td>0.022</td>
<td>no</td>
<td>yes, dense</td>
</tr>
<tr>
<td>28</td>
<td>20% B</td>
<td>23</td>
<td>10</td>
<td>-</td>
<td>0.108</td>
<td>-</td>
<td>0.021</td>
<td>no</td>
<td>several and dense</td>
</tr>
<tr>
<td>24</td>
<td>20% B</td>
<td>23</td>
<td>15</td>
<td>0.044</td>
<td>0.108</td>
<td>0.276</td>
<td>0.025</td>
<td>no</td>
<td>rare and not dense</td>
</tr>
<tr>
<td>25</td>
<td>20% B</td>
<td>23</td>
<td>25</td>
<td>0.051</td>
<td>0.138</td>
<td>0.317</td>
<td>0.029</td>
<td>no</td>
<td>rare</td>
</tr>
</tbody>
</table>

Figure 3.5: Fibers diameters of 20% B solution at different distance tip-to-collector.
3.1.4 Voltage

The applied voltage supply gives a strong electrical force that overcomes weaker surface tension of the polymer solution at certain threshold to eject a liquid jet. This force favors the creation of elongated fibers, in opposition of the surface tension, that produces sphere-like structures.

As it is possible to notice with the SEM images, the increase of the voltage does not influence significantly the fibers structure. The table below shows that the fibers from 10% and 20% B solutions at different voltages maintain a constant diameter for each fiber size. Spider webs are not influenced neither on the amount nor on their size.

A clear interference of the Coulomb repulsion with the fibers structure is shown in 3.1: in 3.2(a) the electric force was not enough strong to overcome the surface tension of the solution, and the sample was constituted only by spheres. Once the surface tension is lower, smooth filaments are created.
3.1.5 Humidity

The ambient relative humidity in the electrospinning chamber played an important part in determining the evaporation speed of solvent in charged droplets during the flight. The low relative humidity accelerated the process, making the fibers being split into spider webs, and the high relative humidity retarded the evaporation of the solvent from jets, with the formation of beaded fibers and droplets. Decreasing the humidity from 50% to 10% brought to a constant increase of the amount of spider webs. Since the evaporation of the solvent is faster, it is the first path of the jet from the Taylor cone with relatively large diameter that solidifies. As it is possible to notice in Fig. 3.9, nanofibers sizes increase when lowering the humidity. As the relative humidity increased to 50%, the structure was homogeneous, without the appearance of spider webs and from 70% to 100% an increasing amount of beaded fibers and droplets were shown.
## Chapter 3. Results and Discussion

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solution %</th>
<th>Age days</th>
<th>Humidity %</th>
<th>Small um</th>
<th>Medium um</th>
<th>Large um</th>
<th>Spider um</th>
<th>Flat ribbons</th>
<th>Spider web</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>20% B</td>
<td>20</td>
<td>10%</td>
<td>0.062</td>
<td>0.170</td>
<td>0.236</td>
<td>0.033</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>41</td>
<td>20% B</td>
<td>20</td>
<td>20%</td>
<td>0.065</td>
<td>0.122</td>
<td>0.228</td>
<td>0.027</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>33</td>
<td>20% B</td>
<td>51</td>
<td>30%</td>
<td>0.059</td>
<td>0.109</td>
<td>0.254</td>
<td>0.033</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>30</td>
<td>20% B</td>
<td>50</td>
<td>50%</td>
<td>0.048</td>
<td>0.112</td>
<td>0.180</td>
<td>-</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>37</td>
<td>20% B</td>
<td>53</td>
<td>70%</td>
<td>0.043</td>
<td>0.095</td>
<td>0.154</td>
<td>-</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>38</td>
<td>20% B</td>
<td>53</td>
<td>100%</td>
<td>0.039</td>
<td>0.090</td>
<td>0.134</td>
<td>-</td>
<td>no</td>
<td>no</td>
</tr>
</tbody>
</table>

**Figure 3.9**: Fibers diameters of 20% B solution at different humidities.
Chapter 3. Results and discussion

(a) RH: 10%

(b) RH: 20%

(c) RH: 30%

(d) RH: 50%

(e) RH: 70%

(f) RH: 100%

Figure 3.10: SEM images of 20% B solution at different humidities.
3.1.6 Feeding rate and needle diameter

The diameter of the spin jet delivered from Taylor cone is not influenced by the needle size or the feeding rate, and so also the fibers diameters. Since the amount of solution split on the collector maintain the same value, the excess of liquid initially forms an increasing drop on the needle and than is sprayed randomly. Droplets of different sizes and large fibers deposited on or covered by fibers are so found on the aluminium foil.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solution %</th>
<th>Age days</th>
<th>Needle mm</th>
<th>Feeding rate ul/min</th>
<th>Small um</th>
<th>Medium um</th>
<th>Large um</th>
<th>Spider um</th>
<th>Flat ribbons</th>
<th>Spider web</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>10%</td>
<td>71</td>
<td>0.40</td>
<td>10</td>
<td>0.030</td>
<td>0.061</td>
<td>0.114</td>
<td>-</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>16.1</td>
<td>10%</td>
<td>71</td>
<td>0.70</td>
<td>5</td>
<td>0.040</td>
<td>0.063</td>
<td>0.090</td>
<td>-</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>16.2</td>
<td>10%</td>
<td>73</td>
<td>0.70</td>
<td>5</td>
<td>0.029</td>
<td>0.054</td>
<td>0.085</td>
<td>-</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>17</td>
<td>10%</td>
<td>71</td>
<td>1.20</td>
<td>5</td>
<td>0.044</td>
<td>0.070</td>
<td>0.107</td>
<td>-</td>
<td>no</td>
<td>no</td>
</tr>
</tbody>
</table>

**Figure 3.11:** Fibers diameters of 10% solution at different feeding rates and needle diameters.
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3.1.7 Types of fibers

A variety of cross sectional shapes and sizes can be obtained from different polymer solutions during electrospinning: circular fibers, branched fibers, flat ribbons, spider webs, beaded fibers and droplets, fibers split longitudinally from larger fibers. Fluid mechanical effects, instabilities of the jet, electric charge carried with the jet and evaporation of the solvent all contributed to the formation of the fibers.

Figure 3.12: SEM images of 10% solution at 5 and 10 µ/l feed rate, and split from 0.7 and 1.2 mm needles.
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(a) Circular fibers
(b) Branched fibers
(c) Flat ribbons
(d) Spider webs
(e) Beaded fibers and droplets
(f) Fibers splitter longitudinally

Figure 3.13: SEM images of 20% B solution at different humidities.

Beaded fibers and droplets
The formation of the beaded nanofibers (see Fig. 3.14(a)) can be considered as the capillary breakup of the electrospinning jets by surface tension, altered by the presence
of electrical forces. For polymer solutions, instead of breaking rapidly, the filaments between the droplets are stabilized and a stable beads-on-string structure is formed. The reason for this is that the coiled macromolecules of the dissolved polymer are transformed by the elongational flow of the jet into oriented, entangled networks that persist as the fiber solidifies. The contraction of the radius of the jet, which is driven by surface tension, causes the remaining solution to form beads. Characterization of the formation of electrospun beaded nanofibers shows that two properties of the solution composed by polymer and solvent (viscosity and surface tension) and one ambient parameter (humidity) are the main factors. Higher viscosity favors formation of fibers without beads, surface tension drives towards the formation of beads, and high relative humidity retards the evaporation of the solvent forming droplets and beads.

Random droplets deposited on the collector are due to a feeding rate too high and a needle diameter too large: the excess of the solution does not enlarge the jet diameter nor creates two jets. It forms an increasing drop down to the needle that is being sprayed forward randomly. Fig. 3.14(b) shows a drop covered by nanofibers.

![Figure 3.14: SEM images of a beaded fiber and a droplet.](image)

**Flat ribbons, split and branched fibers.**
Branched and split fibers were formed by electrical instabilities on the surface of the primary jet. The balance between the surface tension and electrical forces can shift so that the shape of a jet becomes unstable. Such an unstable jet can reduce its local charge per unit surface area by ejecting a smaller jet from the surface of the primary jet, similarly to the ejection of a jet from the surface of a charged droplet, or by splitting apart into two smaller jets.

Fibers in the form of ribbons resulted from a thin skin formed by the rapid evaporation of the solvent. Atmospheric pressure tended to collapse the tube formed by the skin as the solvent evaporated by diffusion through the skin. The circular cross section became elliptical and then flat, forming a ribbon. It could happen that the jet collapsed in such a way that the diametrically opposite parts of the skin come into contact and two smaller tubes are formed, as shown in Fig. 3.15(a) and Fig. 3.15(c). These small tubes remained after all the solvent was gone (dog-bone fiber).
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(a) Collapse of the skin of a fiber.

(b) Branched fiber.

(c) Longitudinally split fiber.

Figure 3.15: Branched and longitudinally split fibers

Nanospider webs

The morphology and area density of spider webs were an overall result of various electrospinning operational parameters, mainly of concentration of the solution, relative humidity and distance tip-to-collector. The typical spider web has nanowire diameter equal to one-fifth that of the average electrospun fiber. The formation of these webs from films is considered to be due to the fast phase separation of polymer and solvent in the charged droplet, caused by solvent evaporation during the flight inside the high electric field before reaching the collector. Another cause could be the break up of a large flat ribbon (Fig. 3.16(a)) or a fiber split longitudinally (3.16(b)) after being elongated and stretched by electric forces.

The ambient relative humidity in the electrospinning chamber played an important part in determining the evaporation speed of solvent in charged droplets during the flight. Lowering the humidity from to 40% down to 10% accelerates the evaporation of the solvent creating denser and more frequent spider webs.

Another operational parameter which affected the spider web formation was the distance tip-to-collector. When the distance is really short (as 5 cm, Fig. 3.6(a)), the spider webs are not dense and the fiber diameter is larger: at this distance only the first part of the jet path can solidify on the collector (see Fig. 1.8), the collecting area is small. Slightly distancing the collector, the jet path is longer, the collecting area bigger and the spider webs are more frequent. Due to the short distance, the spider webs do not have time to fully expand and are thick and dense (Fig. 3.6(b)). As the distance increases, they become larger and less dense, slowly decreasing the frequency.
(a) Broken ribbon.  (b) Longitudinally split fiber.

Figure 3.16: SEM images of a broken ribbon and a longitudinally split fiber that generated a spider web.
3.2 Air Filtration

The following sections show the efficiency and penetration graphs of the filtration tests performed. For every kind of filter, different samples have been studied. Initially a blank filter has been tested, and than it has been compared with the results obtained from the filtration tests of other samples with different kind of fibers split on one surface. The pressure drop of every sample of every kind of filter has been measured.

The set-up apparatus was the same for every filtration test, with the exception of some tests performed on the Paper Filter (more details in the next Paper Filter section).

All filters were tested with 10 cm/s face velocity, except for the last three tests on polyester filters.

The error bars on the graphs correspond to the standard error of the mean of the data collected upstream and downstream the filter.

3.2.1 Glass nanofiber filter

Glass nanofiber filters have been tested with a range of particles between 10 and 450 nm. 3.17 lists the filters tested, the nanofibers and the pressure drop.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Filter Type</th>
<th>Nanofibers</th>
<th>Concentration %</th>
<th>Collecting Time min</th>
<th>Pressure drop Pa</th>
</tr>
</thead>
<tbody>
<tr>
<td>GF - 0</td>
<td>Glass Filter</td>
<td>-</td>
<td>-</td>
<td>3830</td>
<td></td>
</tr>
<tr>
<td>GF - 2</td>
<td>Glass Filter</td>
<td>10%</td>
<td>30</td>
<td>3860</td>
<td></td>
</tr>
<tr>
<td>GF - 3</td>
<td>Glass Filter</td>
<td>20% A</td>
<td>30</td>
<td>3880</td>
<td></td>
</tr>
</tbody>
</table>

Figure 3.17: Tested glass nanofiber filters.

Fig. 3.18 shows the efficiency and the penetration of each tested filter.

Blank glass nanofiber filter was already extremely efficient: between 99.995% and 99.999%. It was intuitable analysing the SEM images (2.8): its surface shows several layers of thick and dense fibers. The pressure drop started from a high value for a blank filter (3830 Pa), and slightly increased with the presence of nanofibers. The increase is proportional to the concentration of the polymer solution. Since the efficiency of the filter without nanofibers split on it is high, it is not possible to verify the improvement due to them. For this reason, glass nanofiber filters were stopped of being used and paper filters have been started to be tested.
3.2.2 Paper filter

Initially, paper filters have been tested with a range of particles between 20 and 450 nm. As it is possible to see on Fig. 3.20(a), the particle size with the lowest efficiency was small, around 50 nm. More tests have been performed in order to verify if the filtration was strongly influenced by electrostatic forces. The neutraliser was used and removed in order to not have any interaction from the electrostatics on the NaCl particles, and the filter was washed with IPA in order to remove the electrostatics from the filters. From the graph it is clear that the electrostatic forces were not influencing the efficiency of the filters.

3.19 lists the filters tested, the nanofibers and the pressure drops.
Fig. 3.20 shows the efficiency and the penetration of each tested filter.

![Graph showing efficiency and penetration of filters](image)

(a) Efficiency of Blank Paper Filters.

(b) Penetration of Blank Paper Filters.

**Figure 3.20:** Results of filtration tests on blank paper filters.

In second phase, paper filters have been tested with a range of smaller particles, between 15 and 150 nm, in order to analyse more in detail the range with the lowest efficiency. 3.21 lists the filters tested, the nanofibers and the pressure drops.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Filter Type</th>
<th>Nanofibers</th>
<th>Concentration</th>
<th>Collecting time (min)</th>
<th>Pressure drop (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PF - 0</td>
<td>PF</td>
<td>A</td>
<td>-</td>
<td>-</td>
<td>5088</td>
</tr>
<tr>
<td>PF - 6</td>
<td>PF</td>
<td>5%</td>
<td>10</td>
<td>10</td>
<td>3100</td>
</tr>
<tr>
<td>PF - 7</td>
<td>PF</td>
<td>10%</td>
<td>10</td>
<td>10</td>
<td>3133</td>
</tr>
<tr>
<td>PF - 8</td>
<td>PF</td>
<td>10%</td>
<td>20</td>
<td>20</td>
<td>3155</td>
</tr>
<tr>
<td>PF - 1</td>
<td>PF</td>
<td>10%</td>
<td>30</td>
<td>30</td>
<td>3160</td>
</tr>
<tr>
<td>PF - 2</td>
<td>PF</td>
<td>20% A</td>
<td>10</td>
<td>10</td>
<td>3154</td>
</tr>
<tr>
<td>PF - 3</td>
<td>PF</td>
<td>20% A</td>
<td>20</td>
<td>20</td>
<td>3196</td>
</tr>
</tbody>
</table>

**Figure 3.21:** Tested paper filters.
The small increase of efficiency of the filter with 5% solution is due to the deposition of the polymer in spherical shapes and not in fibers (See Fig. 3.2(a)). Filters with 10% solutions fibers are less efficient than the ones with 20% A, showing that the improvement of the efficiency is directly correlated with the concentration of the solution. Moreover, for both concentrations, filters with a longer collecting time fibers are better.

Paper filters with 10%, 20 and 30 minutes collecting time fibers and 20% A, 10 minutes collecting time are reaching the same range of efficiency values (between 90% and 96%), but the two samples with 10% solution fibers are more efficient at sizes smaller than 60 nm than 20% A, 10 minutes collecting time.

The pressure drop started from a high value for a blank filter (3088 Pa), and slightly increased with the presence of nanofibers. The increase is proportional to the concentration of the polymer solution and the collecting time.

Fig. 3.22 shows the efficiency and the penetration of each tested filter.
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(a) Efficiency of Paper Filters.

(b) Zoom of efficiency of Paper Filters.

(c) Penetration of Glass Nanofiber Filters.

Figure 3.22: Results of filtration tests on paper filters.

Since paper filters gave the possibility to only test a small range of particles, polyester
filters started to be analysed.

### 3.2.3 Polyester filter

Polyester filters have been tested with a range of particles between 15 and 450 nm, except for a blank filter and a filter with 5% solution split for 10 minutes that have been tested with a range from 50 up to 450 nm. 3.23 lists the filters tested, the nanofibers, the distances tip-to-collector and the pressure drops.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Filter Type</th>
<th>Concentration %</th>
<th>Collecting time min</th>
<th>Distance cm</th>
<th>Pressure drop Pa</th>
</tr>
</thead>
<tbody>
<tr>
<td>RM75 - 0</td>
<td>Reemay 2275</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>RM75 - 3</td>
<td>Reemay 2275</td>
<td>5%</td>
<td>10</td>
<td>15</td>
<td>7</td>
</tr>
<tr>
<td>RM75 - 2</td>
<td>Reemay 2275</td>
<td>10%</td>
<td>10</td>
<td>15</td>
<td>81</td>
</tr>
<tr>
<td>RM75 - 1</td>
<td>Reemay 2275</td>
<td>20% A</td>
<td>10</td>
<td>15</td>
<td>164</td>
</tr>
<tr>
<td>RM75 - 15</td>
<td>Reemay 2275</td>
<td>20% B</td>
<td>10</td>
<td>15</td>
<td>92</td>
</tr>
<tr>
<td>RM75 - 4</td>
<td>Reemay 2275</td>
<td>20% B</td>
<td>10</td>
<td>10</td>
<td>283</td>
</tr>
</tbody>
</table>

**Figure 3.23:** Tested polyester filters (RM 2775).

As for paper filter, the contribution of the 5% polymer solution on the filter surface is negligible, efficiency does not increase significantly. The presence of nanofibers on the filter raised the efficiency at values between 78% and 99.8%.

The improvement of the efficiency is directly correlated with the viscosity of the solution and the distance tip-to-collector. Once the viscosity is high, also the efficiency raises. It is possible to notice it clearly from the filters with 5%, 10% and 20%. Moreover, there is also a difference between 20% A and 20% B solutions. 20% A solution has been created 2 months earlier than 20% B, so its viscosity is lower. The filter with 20% A nanofibers is less efficient than the other. The shorter distance brings to a higher number of nanofibers layers. Indeed, filter with 10% nanofibers is less efficient than filter with 20% nanofibers, and this one is less efficient than filter with 20% nanofibers split from a shorter distance (10 cm instead of 15 cm).

The pressure drop started from a low value for a blank filter (3 Pa), and increased with the presence of nanofibers. The increase is proportional to the concentration of the polymer solution, the distance tip-to-collector and the collecting time. Fig. 3.24 shows the efficiency and the penetration of each tested filter.
Figure 3.24: Results of filtration tests on Reemay 2275 polyester filters.

Three tests have been performed in order to study the effect of the face velocity on the pressure drop and the efficiency. 3.25 lists the filters tested, the nanofibers, the face velocity and the pressure drops.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Filter</th>
<th>Nanofibers</th>
<th>Collecting time</th>
<th>Face velocity</th>
<th>Pressure drop</th>
</tr>
</thead>
<tbody>
<tr>
<td>RM75 - 5</td>
<td>Reemay 2275</td>
<td>20% B</td>
<td>10 min</td>
<td>5 cm/s</td>
<td>57 Pa</td>
</tr>
<tr>
<td>RM75 - 15</td>
<td>Reemay 2275</td>
<td>20% B</td>
<td>10 min</td>
<td>10 cm/s</td>
<td>81 Pa</td>
</tr>
<tr>
<td>RM75 - 15</td>
<td>Reemay 2275</td>
<td>20% B</td>
<td>10 min</td>
<td>15 cm/s</td>
<td>155 Pa</td>
</tr>
</tbody>
</table>

Figure 3.25: Tested polyester filters (RM 2775) tested with different face velocities.
As hypothesised, the filter with the highest efficiency is the one tested with 5 cm/s face velocity, and the filter with the lowest efficiency is the one tested with 15 cm/s face velocity. The pressure drop increased proportional to the face velocity.

Fig. 3.26 shows the SEM images of the filters tested with 5 and 15 cm/s after the filtration: it is possible to see NaCl particles of different sizes. On the first image, the amount of nanoparticles is greater due to the higher efficiency.

![SEM images of polyester filters (5 and 15 cm/s face velocity)](image)

**Figure 3.26:** SEM images of polyester filters (5 and 15 cm/s face velocity).

Fig. 3.27 shows the efficiency and the penetration of each tested filter.
Chapter 3. Results and discussion

(a) Efficiency of Polyester Filters tested with different face velocities.

(b) Penetration of Polyester Filters tested with different face velocities.

Figure 3.27: Results of filtration tests on Reemay 2275 polyester filters with different face velocities.
Chapter 4

Modelling

4.1 Model calculation

The model describes the filter properties and performances, and the air flow behaviour. Aim of work was the calibration of the model, with the penetration curve as objective function. Experimental data were used as inputs and to verify the goodness of the model: the modelled penetration curve of each filter has been compared with the data from the filtration tests.

As inputs, properties of the air flow (particle density, mean free path, viscosity, face velocity), of the substrate (thickness), of the nanofibers (parent fiber size and thickness, spider net fiber size and thickness) have been used.

Calibration task involves systematic adjustment of model parameter estimates so that model outputs reflect external benchmarks more accurately. These parameters have been calibrated: solidity of substrate and nanofibers, number of nanofibers layers, split probability, spider net fracting area, velocity through parent fiber and through spider net fiber, substrate fiber size.

4.1.1 Substrate and nanofibers

The experiment results show the performance of the whole filter: blank filter Reemay 2275 (substrate) and the nanofibers split on its surface. For modelling, these two parts have been studied and modelled separately. Since the different layers are in series, each contribution has been added and the final values have been compared with the experiments results.

**Substrate** is a fiber filter with 0.15 mm thickness. Total efficiency, penetration and pressure drop were calculated with adjusted values of solidity and fiber size. Effectiveness of the model was verified with results of the blank filter filtration test.

**Nanofibers** are considered as a sequel of different layers. On every layer three structures can exist: circular shaped fibers (*parent fiber*), parent fibers split in smaller diameter fibers (*split fibers*) and *nanospider webs*. *Nanospider webs* derive from *split fibers*. 
Their amount (in percentage) is called spider web fracting area $A$. Each type is present on a single layer with a percentage from 0 to 100%. Theoretically it is possible to have layers with all three kinds of structures, with two or with only one.

During the filtration the air flow tends to pass through the parent fibers than the spider webs of the split layer, because the porosity is higher. Thus the face velocity through them would not be the same as the un-split layers. Two different velocities $U_p$ and $U_s$ are found. Fig. 4.1 shows how the air would prefer going through parent fibre than through spider web.

![Diagram of air flow through different layers.](image)

**Figure 4.1:** Air flow through different layers.

### 4.1.2 Implementation

Modelling was based on the fundamental equations of the filtration theory cited in Chapter 1. For each layer, efficiencies of all deposit mechanisms were calculated and the overall efficiency was used in the equation 1.19 to find single layer penetration. Both contributions of substrate and nanofiber layers were considered, and total penetration was found with:

$$P_{total} = P_{nanofibers} P_{substrate}$$

(4.1)

where

$$P_{nanofiber} = (P_{split\ layer} q)(P_{parent\ fiber} (1 - q))$$

(4.2)

and

$$P_{split\ layer} = (P_{spider\ net} A) + (P_{parent\ fiber} (1 - A))$$

(4.3)

with $q$ corresponding to the splitting probability and $A$ to the spider net fracting area.

The pressure drop is depending mainly by face velocity and solidity, and equation 1.22 has been used to calculate the values of each kind of nanofibers. Nanofibers pressure drop is the average of split and of un-split fiber values.

The overall pressure drop is the sum of each contribution:
\[ \Delta p_{total} = (N_{layers} \Delta p_{avg}) + \Delta p_{substrate} \]  

(4.4)

where

\[ \Delta p_{avg} = \Delta p_{split} \, q + \Delta p_{unsplit} \, (1 - q) \]  

(4.5)

### 4.1.3 Results

Fig. 4.2 shows two penetration curves: one resulted from the model and another obtained from an air filtration test performed with Reemay 2275 and 10% solution nanofibers split on its surface for 10 minutes.

![Figure 4.2: Penetration curves: model and experimental data](image-url)

Fig. 4.3 is the result for another air filtration test, performed with Reemay 2275 and 20%A solution nanofibers split on its surface for 10 minutes.
Figure 4.3: Penetration curves: model and experimental data

As seen in the graphs, the experimental and the modelled curves only match partially. Further adjustments on the model will have to be made. This particular work is being performed by the research of Yu-Ying Kuo, EMPA, whose results will be published in her thesis and in a journal paper.
Chapter 5

Conclusion

5.1 Electrospinning

The operational parameters that influence the formation of ultrathin nanofibers are: concentration and age of the solution, humidity and distance tip-to-collector. The first three factors modify the viscosity of the solution, and so the surface tension. This force is a key parameter in the process, and favors sphere-like shapes with smaller surface area per unit mass.

Changing the concentration of polymer solutions brings to different values of viscosity, of which high values brings to the formation of smooth fibers. As the viscosity of the solution is increased, the beads disappear gradually, the shape of the beads changes from spherical to spindle-like and the fiber diameter larger, with formation of flat ribbons.

The older the solution is, the lower is the viscosity, with consequent modifications of the nanofibers structure. The distance tip-to-collector influences mainly the formation of spider webs and the number of layers of nanofibers. Moving the collector closer or further from the needle brings to the solidification of different part of the jet, which is through a straight segment, then through a series of successively smaller electrically driven bending coils.

Voltage is not strongly influencing the nanofibers. The only clearly visible interference of the Coulomb repulsion with the fibers structure can be appreciate when it is lower then surface tension of the solution, and the sample is constituted only by spheres. Once the surface tension is lower, smooth filaments are created.

The ambient relative humidity plays an important part in determining the evaporation speed of solvent in charged droplets during the flight. The high relative humidity retarded the evaporation of the solvent from jets, creating beaded fibers and droplets, and low relative humidity accelerated the process, creating spider webs.

A variety of cross sectional shapes and sizes can be obtained from different polymer solutions during electrospinning: circular fibers, branched fibers, flat ribbons, spider webs, beaded fibers and droplets, fibers split longitudinally from larger fibers.

The formation of the beaded nanofibers can be considered as the capillary breakup of the electrospinning jets by surface tension, altered by the presence of electrical forces. Two properties of the solution composed by polymer and solvent (viscosity and surface tension) and one ambient parameter (humidity) are the main factors. Higher viscosity favors formation of fibers without beads, surface tension drives towards the formation of
beads, and high relative humidity retards the evaporation of the solvent forming droplets and beads. Random droplets deposited on the collector are due to a feeding rate too high and a needle diameter too large: the excess of the solution does not enlarge the jet diameter nor creates two jets. It forms an increasing drop down to the needle that is being sprayed forward randomly. Branched and split fibers were formed by electrical instabilities on the surface of the primary jet, that can eject a smaller jet or split apart into two smaller jets. Fibers in the form of ribbons resulted from a thin skin formed by the rapid evaporation of the solvent. Due to the atmospheric pressure, the circular cross section became elliptical and then flat, forming a ribbon. The morphology and area density of spider webs were an overall result of various electrospinning operational parameters: concentration of the solution, relative humidity and distance tip-to-collector. The formation of these webs from films is considered to be due the solvent evaporation during the flight inside the high electric field before reaching the collector, or due to the break up of a large flat ribbon or a fiber split longitudinally. Lowering the humidity accelerates the evaporation of the solvent creating denser and more frequent spider webs. Modifying the distance tip-to-collector the jet path that can solidify on the collector changes. If the distance is short, the spider webs do not have time to fully expand and are thick and dense.

5.2 Filtration

Nanofibers strongly improve the efficiency of a commercial filter if split on its surface. Since the efficiency of a blank glass nanofiber filter was too high and paper filters gave the possibility to only test a small range of particles, they have been stopped to be used. Studying Polyester filters, the improvement of the efficiency due to the nanofibers has been analysed. It is directly correlated with the concentration of the solution, the collecting time, the distance tip-to-collector and the face velocity. An increase of the efficiency and pressure drop is linked to: high viscosity of the solution, long collecting time, short distance and low face velocity.

5.3 Future developments

The past few years have witnessed an important progress in the applications of electrospun nanofibers. This study shows the capability of ultrathin nanofibers of being used in air filtration field, improving the efficiency of commercial filters from 1-10% up to 90-99%. First of all, more studies are required in order to understand if and how the nanospider webs influence the filtration: are they strong enough to catch a nanoparticle, or are they being destroyed by the flow? Do area density and thickness of the spider webs bring to a more efficient filter?

Secondly, electrospinning technique should be perfected: avoid solution wastes (and so avoid the formation of droplets randomly split on the collector), try to produce uniform nanofibers with diameter below 30nm, and experiment different kinds of solutions and set-up.
An interesting point would be also the precise evaluation of the percentage of the different fiber sizes that are composing the nanofiber substrate. With these data, the filtration contribution of each fiber size could be evaluate in order to have a more accurate filtration model.

Also filtration technique could be improved, and more experimental studies and theoretical modelling are required in order to achieve a better control and knowledge. Different set-up apparatus, face velocity, kinds and size of filters, and kind of particles could be tested.

An interesting study would be the analysis on the filtration of ambient air in different environment (air from an inside room, from outside, with a small or important content of particles). This would be one of the first step to do in order to understand if the filtration with nanoparticles is versatile and it is worthwhile for doing more studies and realize a scaled-up manufacture and commercialization of electrospun nanofibers.
Bibliography


