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Development of melt-spun monofilaments with enhanced bending stiffness for use in inductively heatable polymer stents

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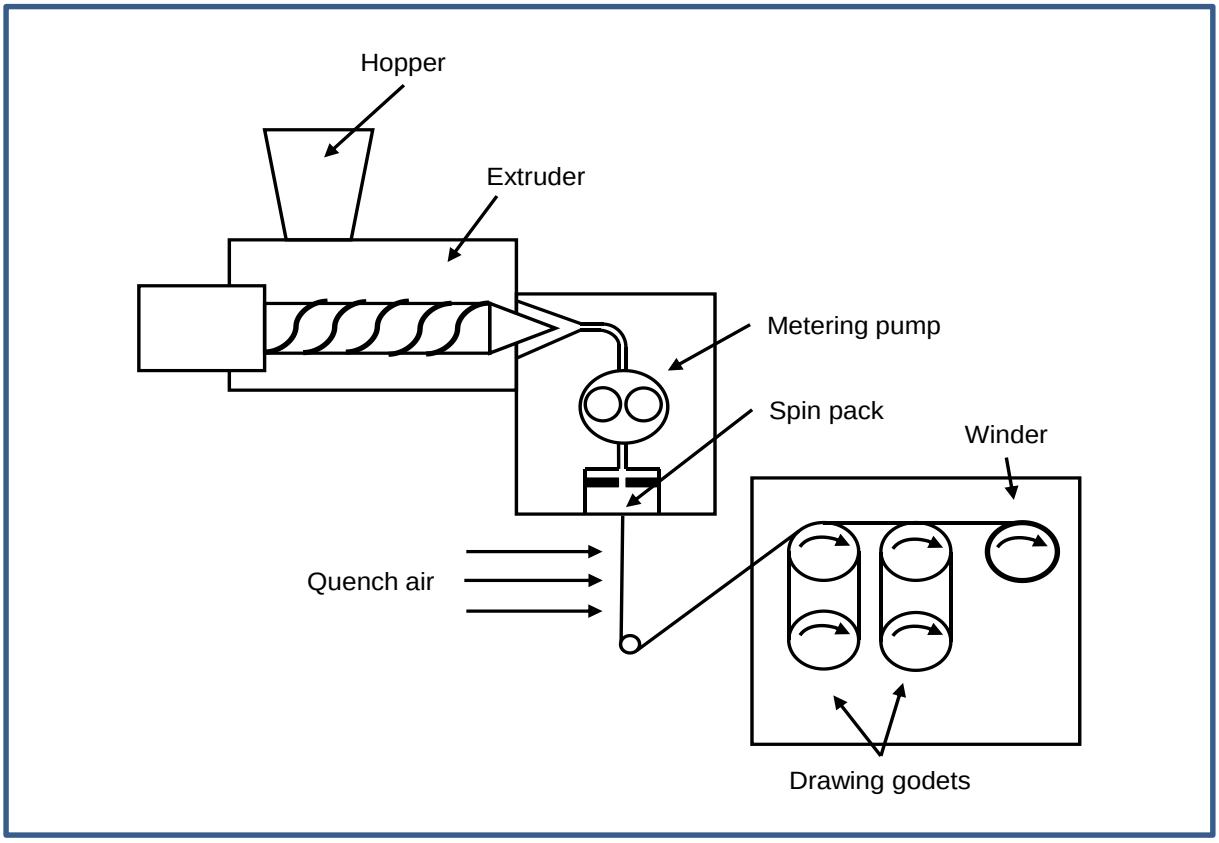

2019

Bachelor Thesis

Development of melt-spun Mono-filaments with enhanced Bending Stiffness for use in inductively heatable Polymer Stents

Diego
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Deutsche Kurzfassung

Ziel der Arbeit: Das Ziel dieser Arbeit ist es, den Herstellungsprozess von Polypropylen-Monofilamenten zu entwickeln, die für die nachfolgende Entwicklung von induktiv aufheizbaren Polymerstents geeignet sind.

Lösungsweg: Die Herstellung eines geeigneten Stents kann durch einen Schmelzspinnprozess mit Polypropylenfasern mit hoher Biegesteifigkeit erfolgen. Um die Stabilität des Prozesses zu gewährleisten und die Optimierung der Parameter zu bestimmen, wird zunächst die OFAT-Methode sowie eine faktorielle Entwurfsmethode durchgeführt, um die Auswirkungen der Parameter auf die Faserproduktion zu bestimmen. Insbesondere werden die Auswirkungen von Ziehverhältnis und Volumenstrom bewertet, um die Anforderungen des Stents, wie Durchmesser und Zähigkeit, zu bestimmen.

Zentrale Ergebnisse: Die Eignung der resultierenden Faser wird durch ihre Biegesteifigkeit bestimmt, die von der Zähigkeit und dem Durchmesser der Fasern abhängt. Um einen hohen Wert der mechanischen Eigenschaften und des Durchmessers zu erhalten, ist ein Gleichgewicht zwischen einem hohen Ziehverhältnis und einem hohen Volumenstrom erforderlich

Schlagwörter: Schmelzspinnen, Garne, Stent, Streckverhältnis, Monofilament

English Abstract

Objective of this thesis: The objective of this thesis is to develop the manufacturing process of polypropylene monofilaments suitable for the subsequent development of inductively heatable polymer stents.

Solution process: The production of an adequate stent can be carried out through a melt spinning process using polypropylene fibers with high bending stiffness. To ensure the stability of the process and determine the optimization of the parameters, a one-factor-at-a-time method is performed, as well as a factorial design method to determine the effects of the parameters on fiber production. In particular, the effect of draw ratio and volume flow are being evaluated in order to determine the requirements of the stent, such as the diameter and the tenacity.

Key results: The suitability of the resulting fiber is defined by its bending stiffness, which is dependent by the tenacity and the diameter of the fibers. In order to get a high value of the mechanical properties and the diameter, a balance between a high draw ratio and a high volumetric flow is needed.

Key word: Melt spinning, Yarn, Stent, Draw ratio, monofilament

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Abbreviations

PP	Polypropylene
DNA	Deoxyribonucleic acid
WHO	World health organization
POL	Polyester
MRI	Magnetic resonance imaging
SPIONs	Superparamagnetic iron oxide nanoparticles
CAs	Contrast agent
AMF	Alternating magnetic field
MMH	Magnetically mediated hyperthermia
DR	Draw ratio
OP	Optical Microscopy
SDS	Stent Delivery System
SEMS	Self-expandable metallic stents

1 Introduction and Objectives

Cancer is the second leading cause of death in the world, only behind cardiovascular diseases [www18a]. If cancer cells begin to spread into the body, they can infiltrate or narrow vessels or hollow organs, such as the windpipe or the esophagus, causing a blockage of these structures and leading to a life-threatening situation. [www19i]

In order to remove the tumor from the affected area, there are many treatments that can be used with this purpose depending on how advanced the disease is. If the cancer is at an early stage and is localized, surgery may be used, otherwise, chemotherapy or radiation therapy are the options. [WHS16]In addition, there are stents, made of metal or polymer, which can be placed in the affected organ or vessel to keep it open. Currently, the most used stents are the self-expandable metallic stents (SEMS) coated with chemicals, due to properties such as flexibility and fracture resistance. [WHS16] [www17c]

However, these treatments present problems and deficits. Cancer treatments have side effects such as tiredness, infections or hair loss. Stents cannot be placed for a long time since the tumor can infiltrate the hollow organ (tumor ingrowth) and the stent again, causing a re-closure and the necessity of restenosis. [www19j] [www19f] For example, for esophageal cancer, over 10 % of cases need a re-stenting. [MPA15]

In this work, the proposed solution is the manufacture of a polymer stent with an adequate radial force by braiding polypropylene fibers with nanoparticles of iron oxide in order to mitigate the mentioned deficits. If the polymer stent is introduced inside a hollow organ, which is infiltrated or narrowed by cancerous tissue, overheating the area through local hyperthermia, the cancerous tissue might be destroyed (Fig. 1.1). By this way, some disadvantages of traditional stents such as the possibility of re-closure could be avoided.

In order to develop a stent to carry out the cancerous tissue destruction, many properties and parameters of the yarns and the spinning process must be examined. The most important property which is necessary to improve is the radial force of the stent since it is the parameter which allows the stent to open the organ and to keep it open. To produce this stent, a monofilament melt-spinning production process will be carried out.

The implementation of this polymeric stent could be an advance in biomedicine and fiber engineering, as a new application of polymer stents could be developed.

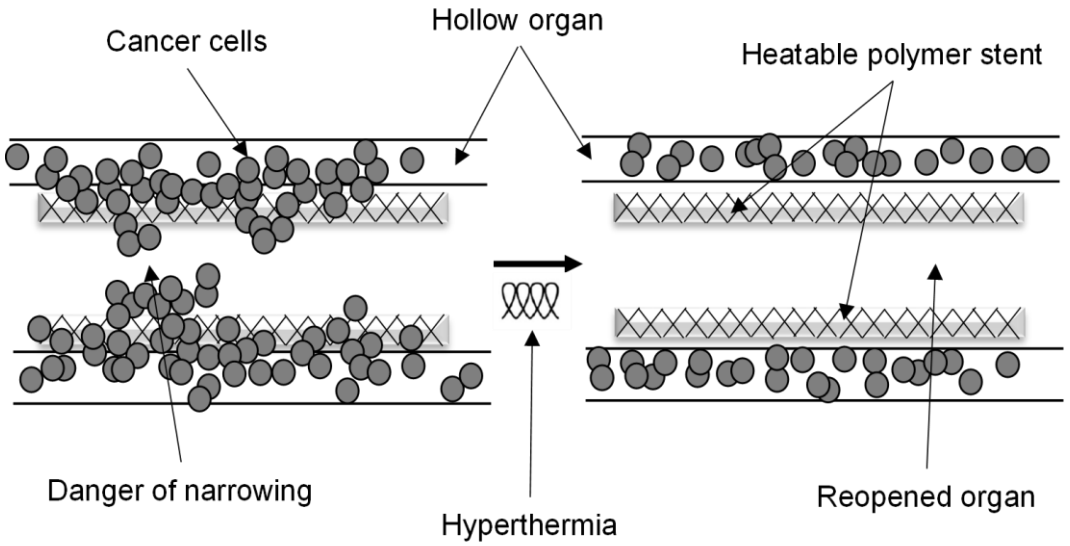


Fig. 1.1: Heatable polymer stent destroys tumor tissue through local hyperthermia

2 Literature Search

2.1 Development of fibers

Fibers are materials with a very high aspect ratio (their length divided by their diameter) between 20 and 60 which vary in diameter from millimeters to nanometers. They can be divided into two types: natural and synthetic. [GBV14]

Natural fibers are produced by plants, animals or geological processes and are normally degradable. Synthetic fibers are made by humans with chemical synthesis and they have usually a cheaper manufacturing and better durability. Some examples of synthetic fibers are polypropylene (PP) and polyethylene (PE). [www16d]

Traditionally the fibers that have been used throughout history are natural, like cotton, wool or silk. However, these fibers have some disadvantages such as its low resistance or the tendency of some fibers to wrinkle, which have led to the need for the development of synthetic fibers to meet the new needs of modern society. The beginning of this development begins at the end of the eighteenth century with the creation of what was then called "artificial silk" and it became more important with the discovery of rayon in 1924, the first manufactured fiber. Since then, man-made fibers has become one of the most studied fields of science and technology. [AnK08]

Currently, there are two trends of fiber-production. One trend is focused on the development of better methods of large-scale production, to be able to manufacture large quantities of fiber in a short time and at a low price. The other current trend is focused on the opposite, in the development of specialized fibers with complex uses. [Hag14]

The second type of production is becoming increasingly important, and its applications range from safety to biomedicine. These are shown in Fig. 2.1.

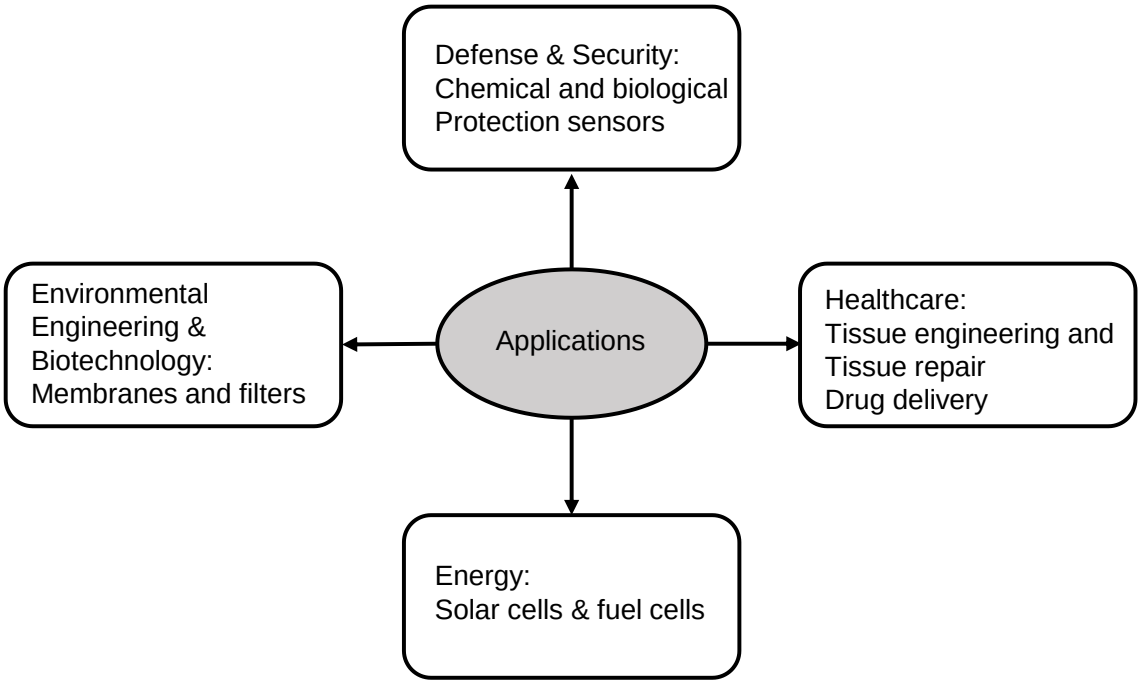


Fig. 2.1: Some applications of polymer fibers [KWT06]

Within these applications, especially the field of biomedicine has increased its market size in recent years, so that the world's major powers are investing more and more money in this type of methods and research. This increase is shown in Fig. 2.2.

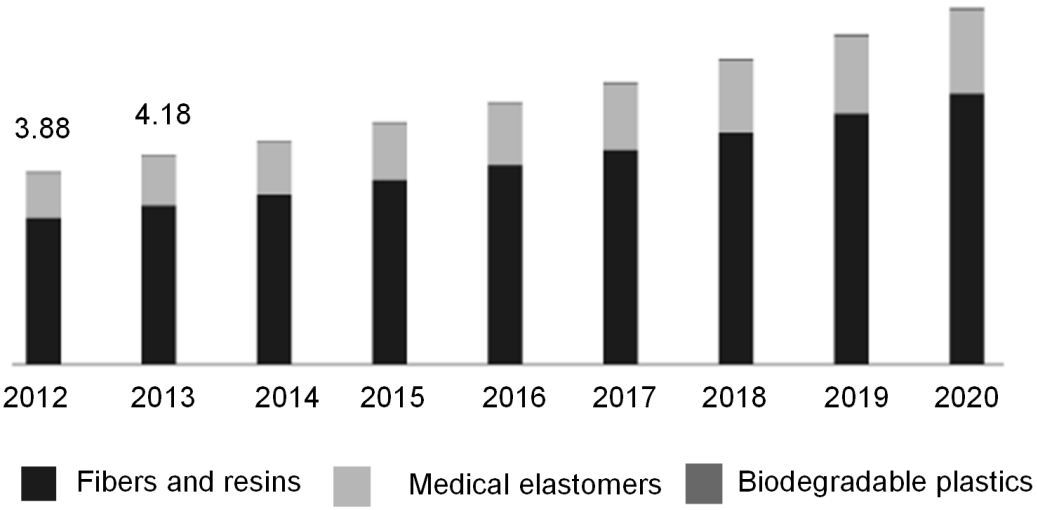


Fig. 2.2: North America medical polymers market size, by product, 2012-2020 (USD Bn) [www17a]

2.2 Melt spinning

In general, fiber spinning is divided into two processes: solvent spinning and melt spinning.

In solvent spinning the polymer is dissolved into a solvent to make a spinnable dope that is extruded into fibers, after which the solvent is removed. There are different variations of this process, such as wet spinning (the oldest), dry spinning and gel spinning.

The other type of fiber spinning is melt spinning. This type of fiber production method has been in use since the late 1950s. This method consists of melting a polymer (normally polyamides, PE, PP, and polyester) in the form of granules that feeds an extruder through a hopper. Next, this molten fluid is pumped through a spinneret under pressure and is solidified and cooled in a cooling chamber. Finally, the resulting filaments are wound into a coil. Normally, the spun filaments lack adequate strength for industrial applications, hence melt spinning is generally followed by a drawing procedure. (Fig. 2.3) [And76]

The spinning speed, the drawing mechanism, and heat conditions are the parameters which most influence the resulting filament. The spinning speed and the drawing system have a great influence on the stress-strain behavior of the fibers, as the orientation of the polymeric chains forming the fibers changes throughout the process, as well as the degree of crystallization. The fiber structure develops as the spinning speed increased. [GBV14]

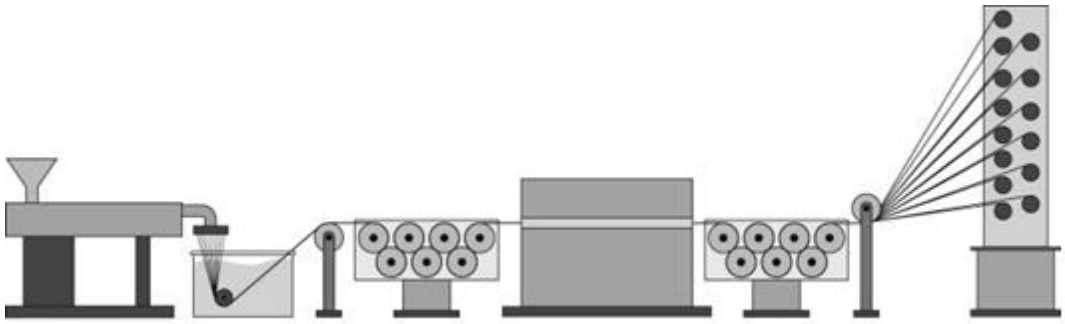


Fig. 2.3: Melt-spinning process [WEH13]

The extrusion velocity is determined by a constant temperature (and pressure) and mass rate, the diameter of the spinneret orifice and the material density. [And76]

Solidification in melt-spinning is due to heat transfer. Cooling can occur in two ways. For multifilaments and thin monofilaments, cooling is done through a cooling chamber between 2 – 5 m long with a gaseous medium, usually air or steam. However, thick yarns are cooled into liquid baths (water) where the heat is transferred faster achieving the solidification of the fiber earlier. However, one disadvantage of the water bath cooling method is that, for large diameters, the extrusion speed decreases. [And76] [Hag14]

Spinning velocities normally range from 30 - 100 m/min (thick monofilaments) to several thousand meters per minute (thin filaments). The mechanical properties of the resultant fibers can be improved by heat-treatment of fibers in the spinline. Through a hot air oven, the fibers heat up and are easily drawn or stretched. Moreover, quenching immediately after finishing the process results in highly oriented amorphous yarns. [GBV14] [And76]

On the one hand, in order to carry out the melt-spinning process, certain requirements must be met [www19c] [And76]:

- The polymer must be fusible and have a melting point.
- The fiber-forming polymer should not be volatile.
- The polymer should not decompose in the molten state.

On the other hand, melt-spinning has some advantages and some disadvantages. The main advantages of this production process are [www19a] [And76] (5):

- High production speeds can be achieved.
- Cost-effectiveness. It is the least expensive spinning method.
- Lack of auxiliary materials (solvents or precipitation agents).
- Does not pollute the environment.

The disadvantages are [www19c]:

- Only thermoplastic polymers are suitable.
- Thermoplastics materials require large heat inputs to raise their temperatures to those required for melt processing.
- Better maintenance of the machine is required compared to other spinning processes.

However, despite the disadvantages, melt-spinning is the most convenient and economical method of fiber manufacturing. [And76]

One of the most used materials are polymers such as polypropylene and polyester since polymers will not suffer thermal degradation at temperatures required to form a melt solution of the desired viscosity. [WEH13]

2.3 Monofilaments

The man-made fibers can be classified into two groups: multifilament and monofilament.

The difference between monofilament and multifilament is that monofilament is a single strand of man-made fiber while multifilament is a yarn with multiple filaments.

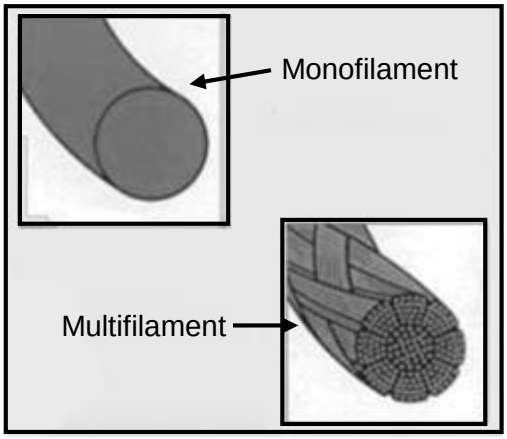


Fig. 2.4: Multifilament and monofilament yarns for suture [www16a]

Each type of filament exhibits different characteristics and properties. For instance, from the point of view of medicine, multifilament suture materials are easier to handle and braid, as well as are more flexible. However, due to braiding and manipulation, pores can be created in their structure where bacteria may lodge causing infections. On the other hand, monofilaments cause less tissue drag and it is harder for bacteria to harbor in surgical sites. [www19b]

For example, bacterial colonization occurs in roughly one-third of all surgical meshes implanted. It is demonstrated that the mesh type and the surgical technique applied have a great influence on the incidence rate of infection. PP meshes show infection rates ranging from 2 - 4.2 %. However, while monofilament POL meshes show infection rates comparable with PP meshes, multifilament POL meshes show the highest infection percentages (7 – 16 %). [GEJ94]

Monofilament extrusion is a process where continuous yarns are produced by extruding a melted polymer through spinneret holes. The melting and extrusion of the polymer are carried out in the same way as a melt spinning process. [Hag14]

The typical spinning setup (Fig. 2.5) consists of an extruder, a metering pump, a spin-pack and a spinneret, a cooling and drawing zone and a winder. This spinning setup is the same for both monofilament and multifilament.

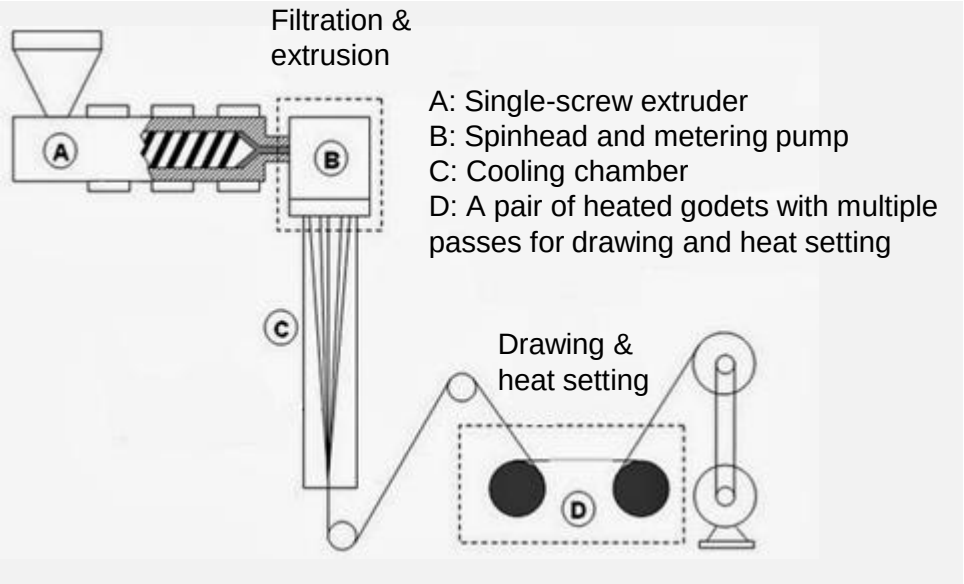


Fig. 2.5: Spinning machine sketch [www19a]

The first important component of the machine is the extruder. An extruder performs multiple functions. First, it extracts the material in granules from the feed system and leads it to the time it compresses it to remove trapped gases such as nitrogen. Second, it mixes and produces a homogeneous melt to ensure continuous spinning without any breaks or non-uniformity in the spun yarns and finally provides sufficient pressure to overcome the flow resistance so that the flow reaches the metering pump. [www19d] A typical design of an extruder is shown in Fig. 2.6.

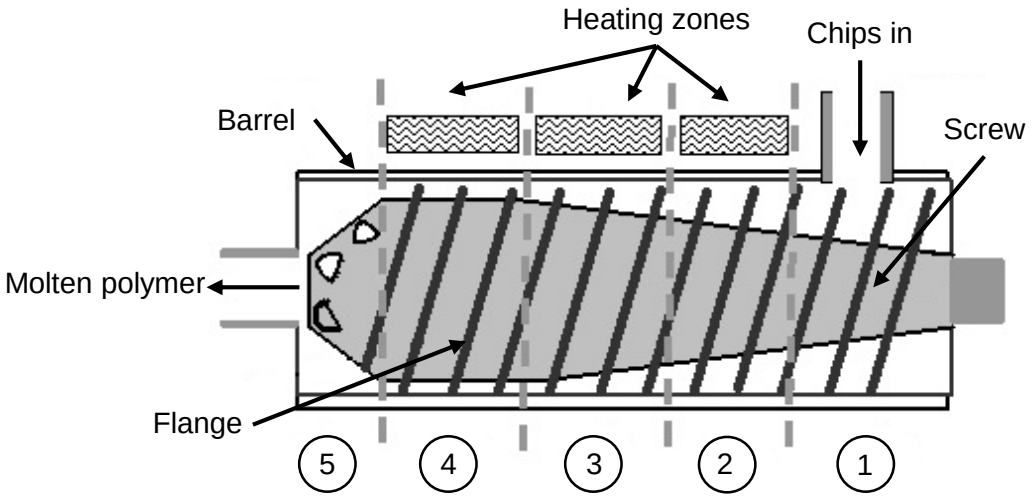


Fig. 2.6: Diagram of extruder [www19d]

The second component of a spinning machine is the metering pump. A metering pump is formed by two gear wheels and regulates the passage of the polymer from the spinneret. Moreover, it must provide a constant flow, and uniform pressure in order to ensure a constant diameter. [www19d]

The following components are the spin pack and the spinneret. The spin pack is the heart of the system. Through a reservoir of polymeric fluid, it removes the solid particles and performs filtration of the molten polymer. A bad filtration can lead to lower flows due to the clogging of the spinneret hole. The main function of a spinneret is to define the cross-sectional shape of the extruded filaments. [www19d]

Finally, the last two components are the cooling chamber, which allows the solidification of the fiber through a cooling fluid (normally water), and the winder, which coils the final yarn.

As mentioned in the previous section, the manufacture of monofilaments by melt spinning requires the use of thermoplastics. Within this type of polymer, the most common for this type of applications is polypropylene. In addition to not suffering thermal degradation, the reasons for which this polymer is the most used are basically its low cost and its easiness to be extruded. [Hag14]

For the spinning of monofilaments, it is very important that the pressure of the extruder and the pump remain constant, otherwise, the process will not be stable. For this, there is a pressure controller that allows keeping this pressure constant. The polymer flow through the spinneret must be constant during the process to ensure that the final diameter of the filaments is constant. To do this, the pump can increase the pressure in the polymer stream to the necessary level and keep it in a uniform value. High pressure across the spinning holes is one of the keys to achieve suitable fiber properties and affects both the molecular orientation and the diameter. [Hag14]

After extruding the polymer, the filaments must be cooled or quenched. Here is the main problem of this type of spinning, since as explained in the previous section, for small filament diameter, they can be cooled in air chambers, like multifilaments, but to get bigger diameters (> 100 μm), they must be cooled in a water bath with typical spinning speeds in the range of 30 – 10 m per min. [And76]

Finally, once the filaments are extruded, they remain highly disoriented and need to be stretched for toughness. The maximum tensile strength and maximum tenacity are achieved when the polymer chains that form the fiber are aligned along the filament axis in the same direction. [WEH13] To achieve this, the fibers are drawn through a drawing system with the aim of orienting these chains and achieving a highly oriented fiber. The filaments then pass through a hot air furnace to facilitate stretching. After stretching, most polymers need second heating to a temperature that crystallizes the filaments.

The last step, after the drawing through the rolls, is the winding of the filaments on tubes or spools.

A typical tensile stress-strain curve for a thermoplastic polymer is shown in Fig. 2.7, with the different stages in the drawing process. [WEH13]

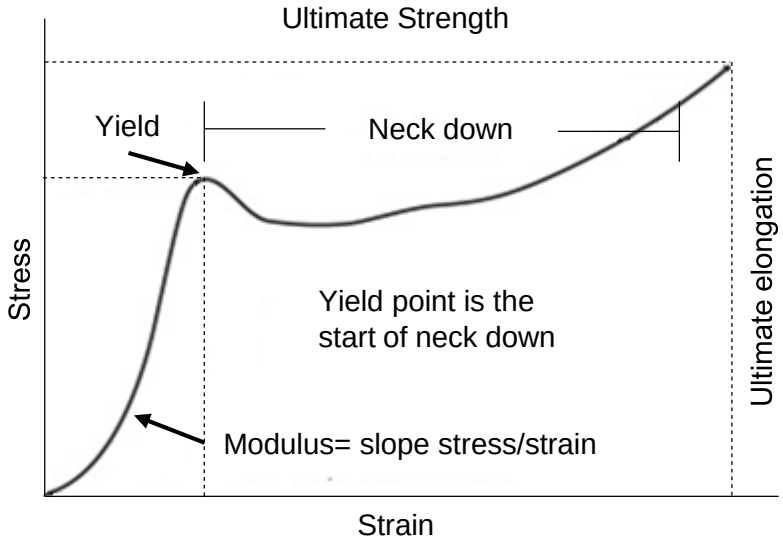


Fig. 2.7: Tensile stress-strain curve [WEH13]

In addition, the polymer chain mobility can be increased by applying heat during the drawing process (for instance the oven heat), facilitating the drawing of the fibers. Therefore, the drawing process is essential to obtain adequate tenacity and diameter.

2.4 Cancer

2.4.1 General

According to the world health organization (WHO), cancer is still killing around 9 millions of people each year, being the second leading cause of death globally, only behind cardiovascular diseases. In Fig. 2.8, the comparison of the causes of deaths between today and 1900 can be seen. [www18a]

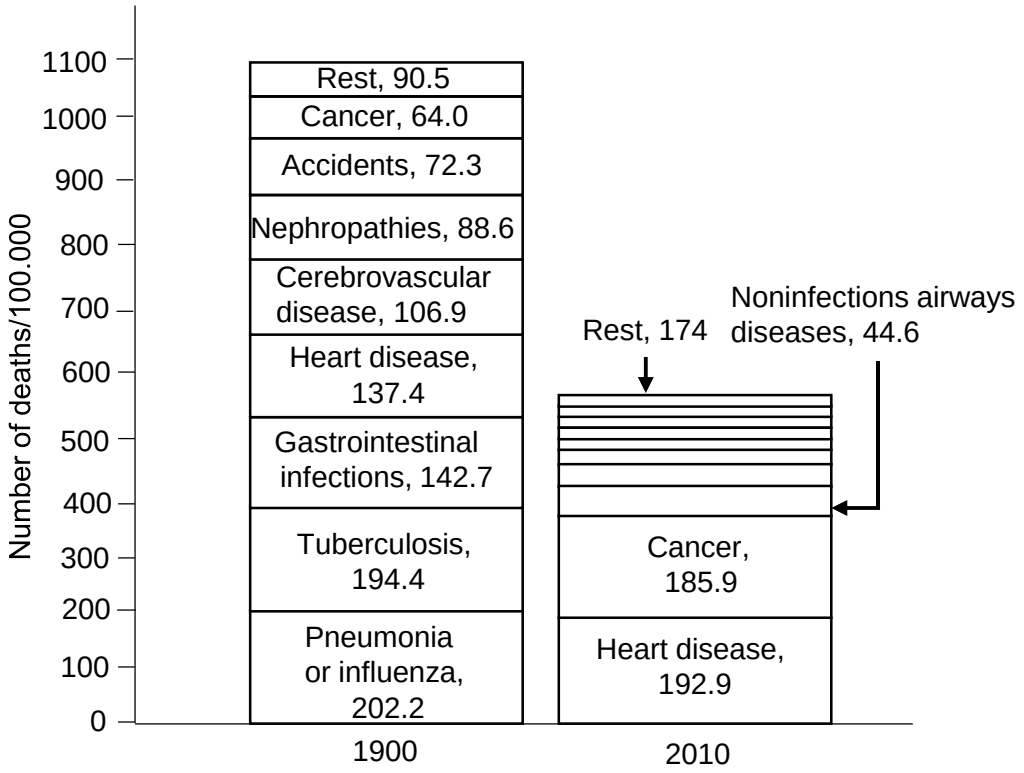


Fig. 2.8: Historical changes in causes of death [GSh12]

The term cancer encompasses a large group of diseases characterized by the development of abnormal cells, which divide and grow uncontrollably in any part of the body.

Cancer causes a change in the normal functioning of the cells that make up the human body, which is as follows: when cells aged or damaged, they die and new cells take their place. Cancer begins when genetic changes interfere with this orderly process. Cells start to grow and divide uncontrollably forming unnecessary cells, which can form a mass called tumor, which can spread to surrounding tissues and organs. [www15a]

Cancer cells, unlike normal ones, are invasive and have many differences with the others. For instance, one of these differences is that cancer cells are less specialized than normal cells, which means that these malignant cells continue to divide without stopping instead of focussing on one function. [www15a]

A scheme of how cancer works is shown in Fig. 2.9.

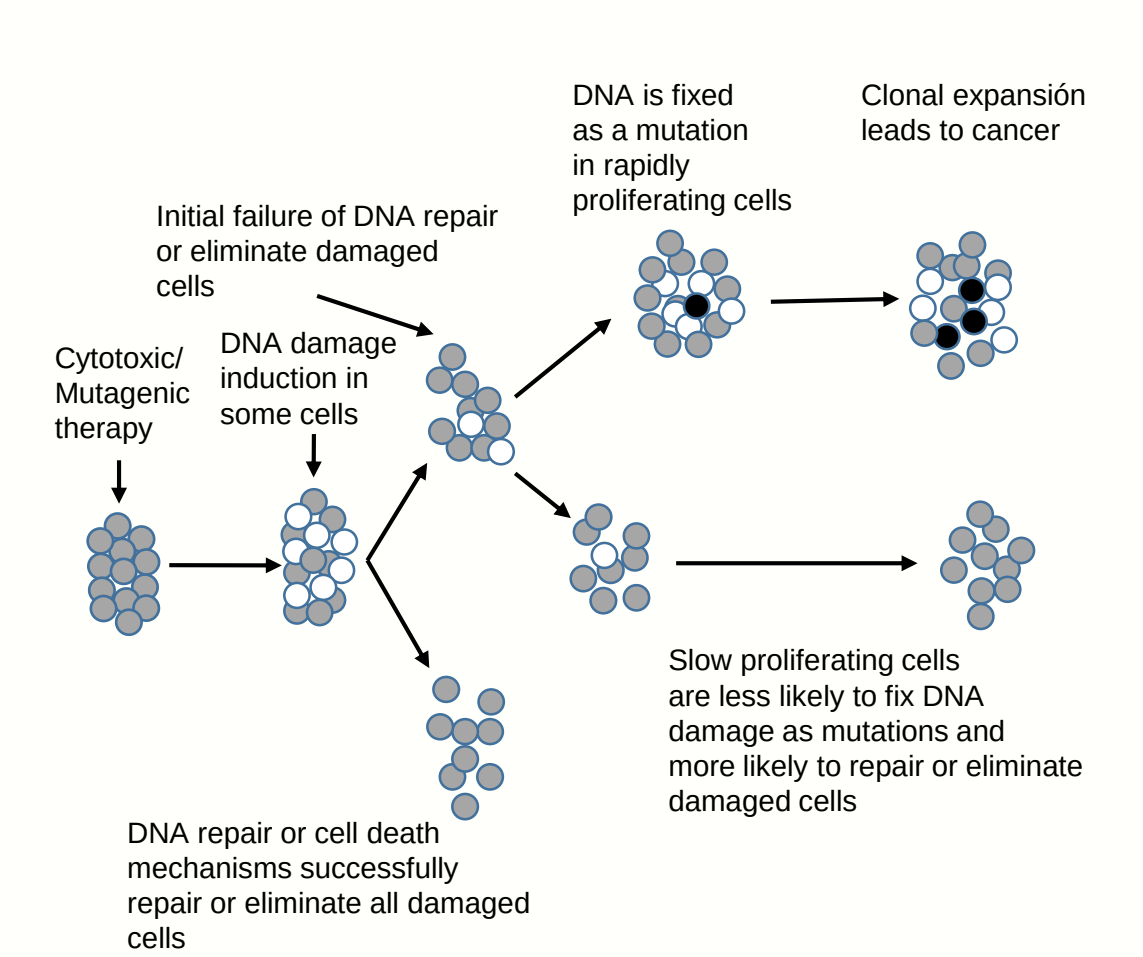


Fig. 2.9: How cancer works (scheme) [www11a]

It is also important to notice that cancer is a genetic disease, this implies that it is caused by changes in genes, which can be inherited from our parents. Moreover, the cancer cells can also arise during a person´s life because of errors that caused damage to DNA. However, the main cause of cancer is not because of genetics (5-10%). Cancer can arise due to bad habits or because of the exposure to some substances such as tobacco, alcohol or radiation. [www15a] In spite of this, according to the WHO, the number of people affected by cancer can be reduced by changing 5 leading behavioral and dietary risks: high body mass index, low fruit and vegetable intake, lack of physical activity, tobacco use, and alcohol use.

The causes of the appearance of cancer can be shown in Fig. 2.10.

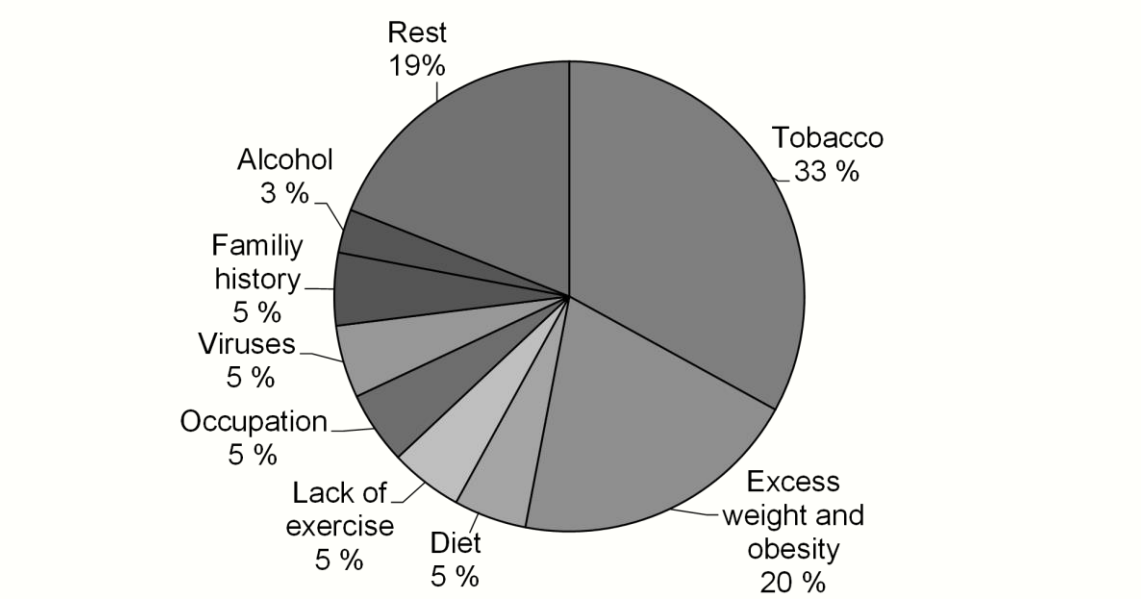


Fig. 2.10: Estimated Percentage of Cancer Caused by Identifiable and/or Potentially Preventable Factors [www15c]

2.4.2 Cancer treatments

There are some treatments to fight cancer. These treatments depend on the type of cancer you have and how advanced it is.

By looking at how advanced the cancer is, the time when the disease is detected can be divided into 4 stages. (Fig. 2.11)

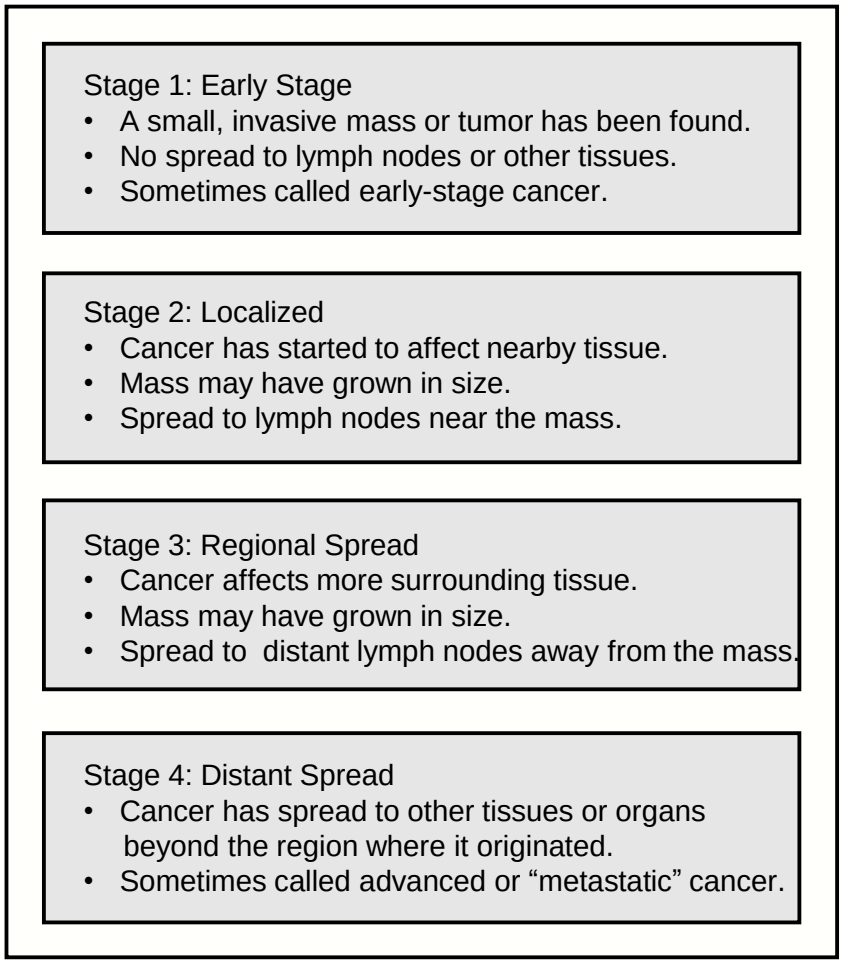


Fig. 2.11: Stages of cancer [www16b]

The most typical types of treatment are:

1. Surgery: Surgery is one of the main treatments for cancer. Surgery is a local treatment (it only treats the part of the body operated on), in which a surgeon removes cancer from the body. So it may remove cancer that is completely contained in one area and has not spread. The earlier a cancer is found the easier it is to remove it.

   Surgery might not be the best treatment for cancers that have spread. It may be better to have a treatment able to reach all parts of your body, such as chemotherapy. Moreover, surgery is not adequate for some types of cancer of the blood system (leukemia). Sometimes, surgery is not possible because of the position of the tumor, especially when tumor is near a blood vessel or other delicate tissue, it can be dangerous to try to remove it. [www15b] [www19f]

   About 45% of patients are treated with surgery to remove their tumor, but a different percentage emerged if the stage of diagnosis is taking into account. About 70% of patients diagnosed at stage 1 undergo surgery, while only 13% of that diagnosed at stage 4. This is because in stage 4, the tumor is widespread and surgery cannot be performed. (Fig. 2.12) [www19e]

   The main risks of surgery are bleeding, pain and infection. These side effects are very common, and practically everyone suffers from them after surgery. However,

there are many ways to deal with them, such as medicines and take care of hygiene. [www19k]

2. Radiation Therapy: It is a cancer treatment that used high doses of radiation to destroy or damage cancer cells to prevent their growth. At high doses, radiation kills cancerous cells or slows growth by damaging their DNA. Once these damaged cells die, the body removes them. [www15b]

   Radiation also affects normal cells. This can cause side effects in the treated area. These most common side effects are tiredness and weakness, sore skin and loss of hair. [www19f]

   There are two main types of radiation therapy: external radiation (radiations comes from a machine that aims radiation at your cancer) and internal implants (a source of radiation is put inside the body). [www15b]

3. Chemotherapy: It is an anti-cancer drug treatment. Chemotherapy works by stopping or slowing the growth of cancer cells. It is used to treat cancer or ease symptoms. [www15b]

   Chemotherapy circulates throughout your body in the bloodstream. So it can treat cancer cells that have spread throughout the body, which is known as systemic treatment. This treatment kills cells that are in the process of splitting into two new cells. [www19f]

   On the other hand, chemotherapy also kills or slows the growth of healthy cells. This damage to healthy cells may cause side effects, such as fatigue, mouth sores, nausea, or hair loss. All these side effects will disappear once the treatment is over and the cells divide properly again. [www15b]

   About 29% of patients need this treatment. In contrast to surgery, only 12% of patients diagnosed at the first stage are treated with chemotherapy, as well as 39% of those treated in the fourth stage. (Fig. 2.12) [www19e]

4. Immunotherapy: This is a cancer treatment that stimulates the body´s natural defenses (immune system) to fight cancer. It uses substances produced by the body or made in a laboratory to improve or restore immune system function. Immunotherapy may work: by stopping or slowing the growth of cancer cells, by stopping cancer from spreading to other parts of the body or helping the immune system work better at killing cancer cells.

   There are several types of immunotherapy. The types are: checkpoint inhibitors (drugs that make the immune system respond more strongly), adoptive cell transfer (attempts to boost the natural ability of your T cells to fight cancer), monoclonal antibodies and treatment vaccines (fight cancer by boosting your immune system´s response to cancer cells). [www15b]

   The most common side effects are skin reaction at the needle site. These side effects include pain, soreness, rash, or fever. [www19f]

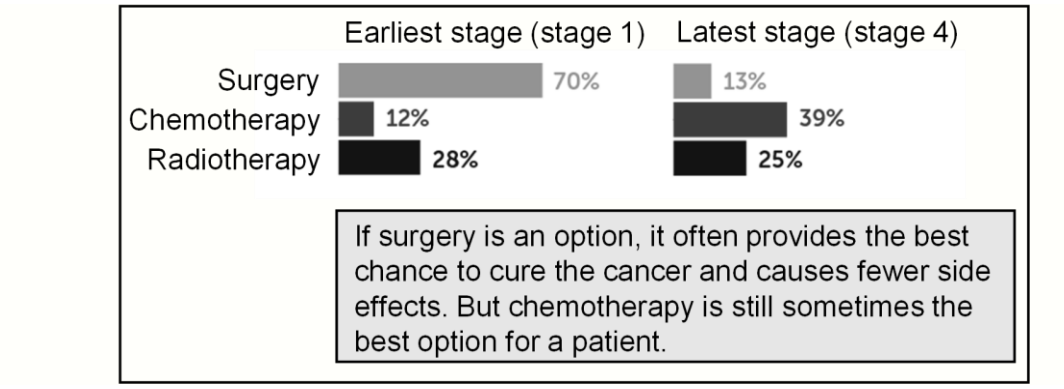


Fig. 2.12: Cancer statistics treatment. [Ste17]

Because of all these treatments, cancer is becoming increasingly curable over the years. This can be seen in Fig. 2.13, where mortality from all cancers in Germany is shown.

Fig. 2.13: Cancer mortality rate in Germany evolution [www14c]

2.4.3 Iron oxide nanoparticles

Metal oxide nanostructures can present unique physical and chemical properties. Some of the most widely used nanoparticles are TiO_2 (titania), ZrO_2 (zirconia) or Fe_2O_3 and Fe_3O_4 (magnetic iron oxides). These materials present good properties (good stability, biocompatibility, and antioxidant) for several biomedical applications such as cancer therapy, drug delivery or therapeutic and diagnostic agents. [SSR18]

The loss of electrons in iron oxide produces different oxidation states such as FeO (II), Fe_2O_3 (III) and Fe_3O_4 (II and III). In particular, maghemite (Fe_2O_3) and magnetite (Fe_3O_4), are the most ordinarily used magnetic materials for biomedical applications. [MSJ18]

On the one hand, one application of metal oxide nanoparticles is hyperthermia treatment (Fig. 2.14), using a magnetic field to heat up magnetic nanoparticles.

Treating cancer via hyperthermia consists of heating the cancer tissue at 41 – 46 °C. This treatment, in conjunction with radiation and chemotherapy, has resulted in synergistic effects to increase the efficacy of conventional treatments and has allowed reducing toxic side effects. [AZI16] Patients who received chemotherapy plus hyperthermia had prolonged median survival rate of 15.4 years compared with those who received only chemotherapy (6.2 years). [www18c]

In magnetically mediated hyperthermia (MMH), the heating of tissue is generated by magnetic nanoparticles in the presence of an alternating magnetic field (AMF).

As a result, the temperature of tumor cells increases. Due to poor vascularization, tumor cells are more sensitive to heat compared to normal cells, leading to a drastic decrease in the survival rate of tumor cells by increasing temperature (Fig. 2.15). [AZI16]

One advantage if this application is that the tumor cells are destroyed without destruction of neighboring healthy cells.

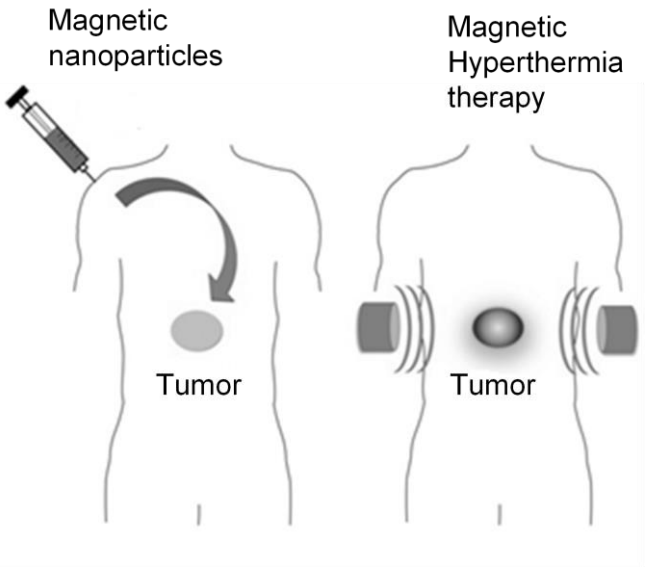


Fig. 2.14: Magnetic hyperthermia [AZI16]

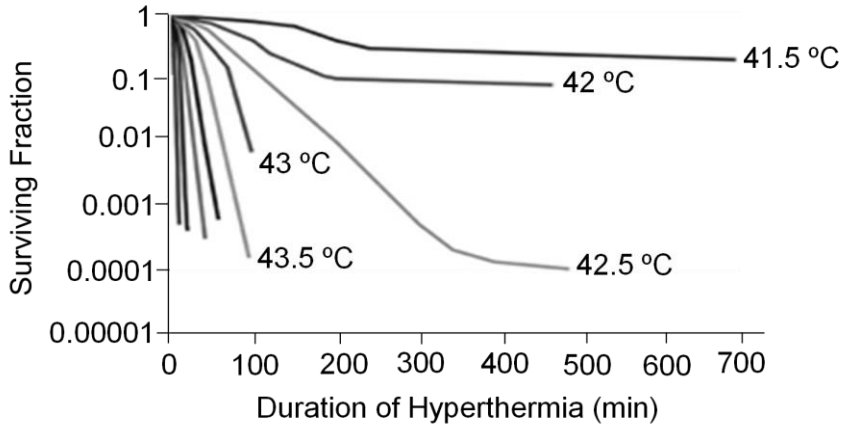


Fig. 2.15: Survival rate of cancer cells according to temperature and time [DMJ18]

On the other hand, magnetic resonance imaging (MRI) is one of the most common biomedical imaging modalities in cancer diagnosis and therapy. Some of the typical imaging methods, such as X-rays, can lead to misdiagnoses due to the reduced contrast quality. However, MRI can solve these problems due to their great contrast capacity to visualize organs and tissues. Even so, deficits of MRI such as its low spatial resolution, its small depth of penetration and its limited sensitivity (a problem for the diagnosis of cancer in early stages) make the application of contrast agents (CAs) necessary. Innovations in nanomaterials have allowed an improvement of contrast agents to resolve these problems. [SJT18]

A category of nanoparticles widely used in MRI as a contrast agent is superparamagnetic iron oxide nanoparticles (SPIONs), which have been investigated for their promising biomedical applications such as targeted drug delivery in tumor therapy. [MSB11] SPIONs possess some advantages over typical CAs. Some of them are superior detection sensitivity, greater biocompatibility and reduced toxicity, and longer retention time.

The magnetic properties of SPIONs represent a real alternative CA, due to the strong shortening effects and its high biocompatibility. Moreover, iron oxide is easily degradable and therefore useful for in vivo applications. [SJT18]

Due to the overcoming of drawbacks of MRI, many studies testing SPIONs with multiimaging modalities have recently described successful visualization improvement. [SJT18]

2.5 Polymer stents

The field of stents has been developing since the creation of the first stent by Charles Dotter in 1980s. He opened the way for interventional cardiology through the design of the first vascular stent. For this, he introduced plastic tubes and collapsible stainless-

steel prosthesis into arteries of dogs. Since then, in the 1990s, vascular and polymer stents have been the main target application of fibers in biomedicine. [www19g]

Recently, the international market for stents has increased greatly, as shown in the Fig. 2.16.

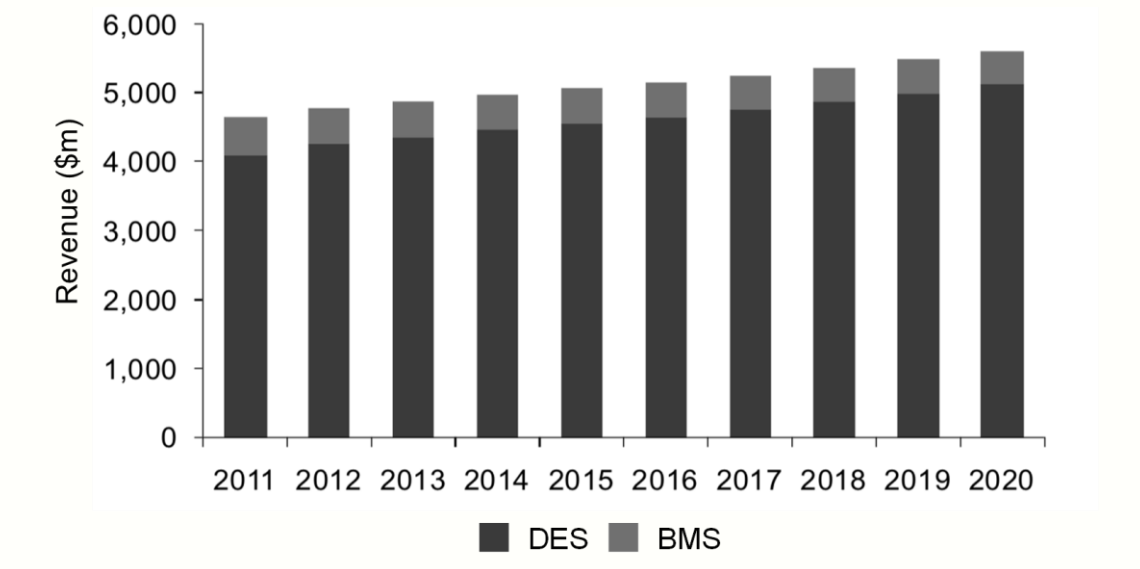


Fig. 2.16: Global Coronary Stents Market Revenue ($m) by type of stent, 2011-2020 [BD14]

A stent is a small and tubular support that is placed temporarily inside a blood vessel, organ, or artery that has been closed or blocked in order to reopen it and keep it open. Sometimes a coronary artery can become narrowed or blocked by a clot, reducing blood flow and causing chest pain. If the formed clot completely blocks the blood flow to the heart muscle, a heart attack results. [www18d] Therefore, stents help keep coronary arteries open. In cancer, stents are used similarly. When the cancer cells infiltrate or narrow a hollow organ, after removing the tumor by surgery (if it is possible), a stent is introduced in the organ to keep it open.

How a stent is and how it works can be seen in Fig. 2.17.

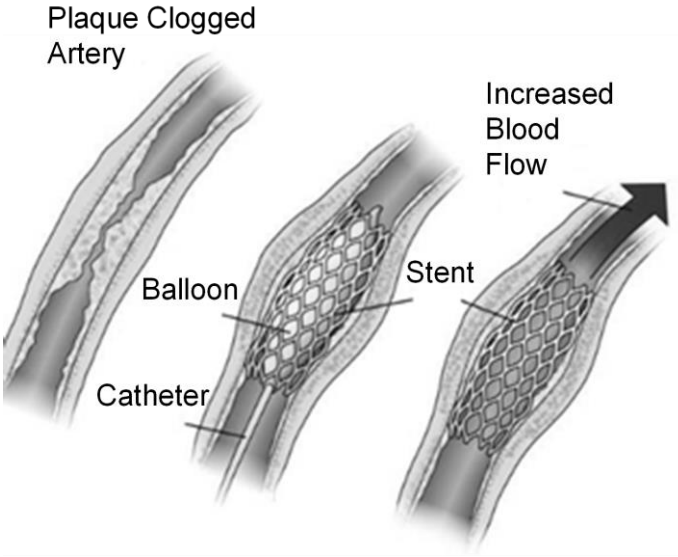


Fig. 2.17: Operation principle of a stent [www19h]

There are three main types of stents: Bare metal stent (BMS), drug eluting stent (DES) and biodegradable stent.

- Bare metal stent: They were the first stents. Despite the good results, in about 20-40% of cases in-stent-restenosis occur. They are generally formed from biocompatible metals such as stainless steel or tantalum, trying to achieve a balance between a high strength to hold the vessel and small thickness to avoid blockages of blood flow. The main problem is that there is a high risk of re-narrowing near to 10-15% and thrombosis can appear, as well as they cannot keep these tubular structures open in the long time [www16c]. Moreover, such stents do not provide to the treated area the delivery of localized therapeutic pharmacological treatment of a blood vessel, which can be useful for overcoming such problems. [SJN15] [PKB97]
- Drug eluting stent: DES are coated with medication that is released (eluted) to help inhibit tissue growth. The released drug can block cell proliferation, ensuring good blood flow and reduces the chances of the artery re-narrowing or restenosis, which is reduced to around 2-3%. [www11b] [www16c]
  In 2010 around 75% of the implanted stents in coronary interventions were DES and only 25% BMS.
- Biodegradable stents: These devices are made of biodegradable polymers that degrade slowly, allowing the artery to remain open long enough for it to recover and return to proper function. A critical factor to consider is the optimal degradation rate, which depending on the material components, varies from six months to over 24 months. However, these stents have not good mechanical properties, being weaker compared to metal. Moreover, this type of stents has another big

disadvantage. Recently, studies have found out that after three years of the introduction of the stent, over 10% of patients experienced a heart attack, the double rate that with metal stents.

The problem was discovered when the researches started to analyze the microstructure of the stents, and they found that at the microscopic level, polymer stents have a heterogeneous structure that eventually leads to structural collapse, causing a loss of integrity of the structure when the stent is inflated. The reason for this collapse is that, while the outer layers of the stent have a smooth crystalline structure made of highly oriented polymers, the inner core tends to have a less ordered structure. [www18b] [SJN15]

An overview of the amount of cardiovascular treatment in Germany from 2005-2013 is shown in Fig. 2.18. It is also remarkable the increase of DES and the decrease of BMS due to the characteristics explained before.

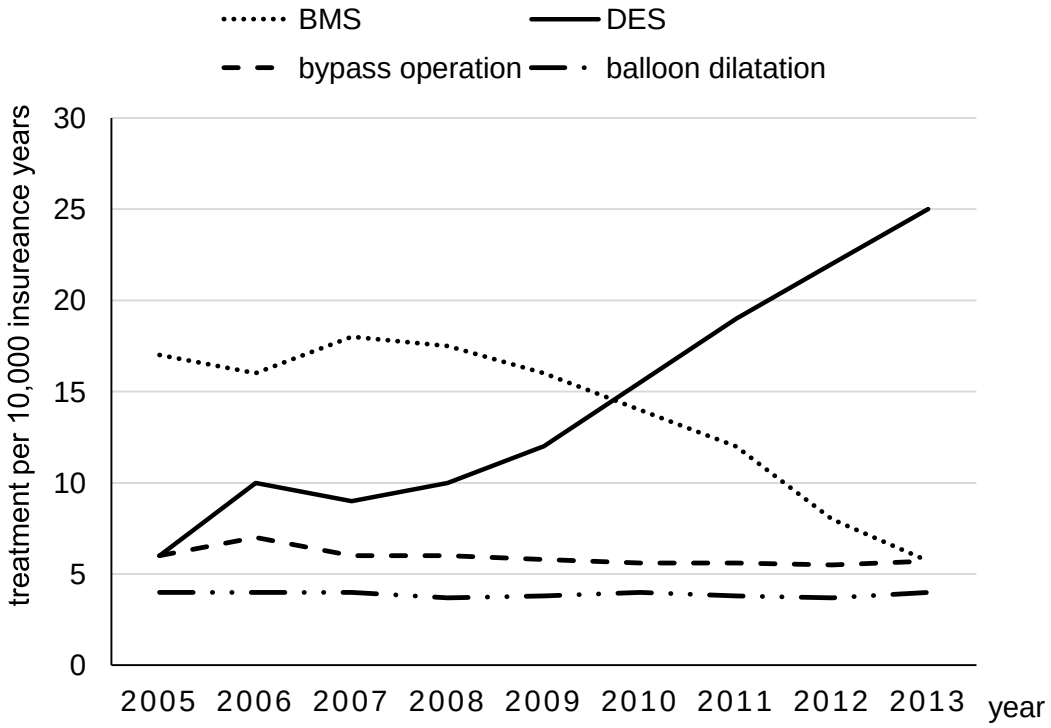


Fig. 2.18: Amount of cardiovascular treatment in Germany from 2005-2013 (per 10000 insurance year) [SJN15]

As mentioned before, these stents have also an important role in cancer therapy. When cancer is spreading out, the tumor cells can infiltrate or narrow hollow organs or vessels, such as the windpipe or the esophagus. Moreover, in 30 % of cases of lung cancer, these cells can invade the airways leading in central airway obstruction and in respiratory distress. [HKH10]

To clean these structures from tumor cells, depending on how advanced the cancer is and the area of application, one or other treatment can be used. For localized cancer and cases where tumor cells have invaded a hollow organ, surgery could be the best option, however, for advanced cancers or lung cancer (vessels and tissues are delicate), surgery is not effective and other treatments such as chemotherapy or radiation should be used. In order to keep these organs or vessels open, a stent can be used. For this type of application, nowadays, the most common stent is self-expanding covered or uncovered stent. [WHS16]

These stents (used also in coronary applications) have properties such as exceptional flexibility, a balanced radial force, an excellent deployment accuracy, and fracture resistance. [www17c] Moreover, such stents are usually made of metal and coated with chemicals to prevent tumor ingrowth. The most typical chemical is Nitinol. [MYK17]

However, self-expandable metallic stents (SEMS) have some problems. Hemorrhaging, perforation, fever or pneumonia are reported in 22 % of cases. [MYK17] But the most important problem is the tumor ingrowth. Tumor cells can infiltrate the stent once it is placed, leading in restenosis and obstruction of the organ or vessel. This affects 10 % of people who have a stent. [MMM17] A solution, apart from the covered with chemicals, could be increasing the diameter, however, the risk of stent-related complications would increase too. [MYK17]

All these problems show how stent therapy is not perfect and have still some problems, making stents not adequate for long time solutions. Maybe, treat the affected area by local hyperthermia through a heatable inductively stent could be the solution.

2.6 Testing methods for bending stiffness

2.6.1 General

The coronary artery and cancer therapy stents have been increasingly used over the past decades for coronary artery and cancer stenosis.

Due to the fact that the radial force of the stent is the parameter which allows the stent to open the organ and to keep it open, the relationship between radial stiffness and stent structures has been widely investigated through the use of several testing devices. [KMT05]

The stiffness of some fabrics is the basic characteristic that determines their suitability for a specific use. Stiffness is one of the most widely used parameters to judge bending rigidity and fabric handling. Fabric stiffness and handling are an important decision factor for end users. The degree of fabric stiffness is related to its properties such as fiber material, yarn, and fabric structure. [BAV14]

Rigidity is generally defined as the resistance of a material against strain under the influence of different forces such as compression, uniaxial tension, bending, simple shearing or vibration. It is a function of Young´s modulus (E) and of the moment of inertia (I) of the material, and it can be calculated with the following equation:

$$G\ (N \cdot m^2) = E \cdot I \tag{2.1}$$

Isotropic materials are characterized by one Young´s modulus, while for anisotropic materials (textiles), the number is higher than one. [BAV14]

2.6.2 Testing methods for fabrics

1. ASTM D4032-02, Standard test method for measuring fabrics stiffness by the circular bend procedure:

   This is a method of multidirectional force action to a specified strain. By means of a digital pneumatic system, stiffness is measured. To do this, through a hole in the test table, it is necessary to previously measure the maximum force of a mandrel causing a simultaneous multidirectional deformation of the fabric. This digital pneumatic is shown in Fig. 2.19. [BAV14]

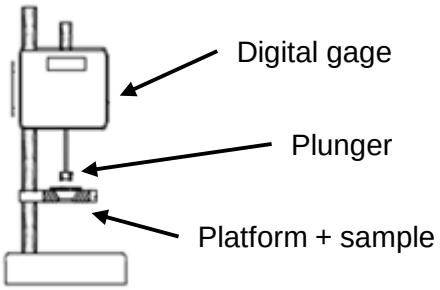


Fig. 2.19: Digital pneumatic stiffness tester [BAV14]

2. Cantilever test:

   This test was proposed by Pierce. It simply involves allowing a 1-in-wide strip of fabric to project as a cantilever from a horizontal platform and measuring the angle between the horizontal and the rope [Nja51]. By pressing the specimen with its own mass until the line joining the top to the edge of the platform forms an angle of 0.724 rad (41.5 º), the length of the overhang is measured.

The bending length and flexural rigidity are calculated from this length. [www11c] (Fig. 2.20)
There are two parameters to calculate from this angle, θ: the bending length, which can be calculated through the following equation:

$$C = l * f(\theta) \tag{2.2}$$

Where l is the length of a fabric overhanging the platform, and f(θ) with the next equation:

$$f(\theta) = (\cos 0.5 \cdot \theta / 8 \cdot \tan\theta)^{1/3} \tag{2.3}$$

Finally, the flexural rigidity:

$$G = w \cdot c^3 \tag{2.4}$$

Where w is the weight per unit area of fabric. [Nja51]
When l is in cm, c is in cm; and when w is in mg. per cm^2, G is mg. cm. This is a reasonable unit for most fabrics.

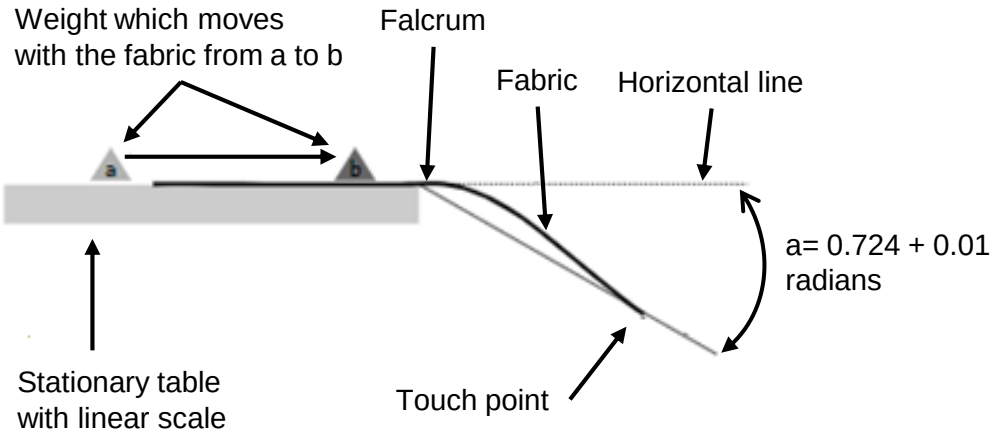


Fig. 2.20: Fabric in bent position [www11c]

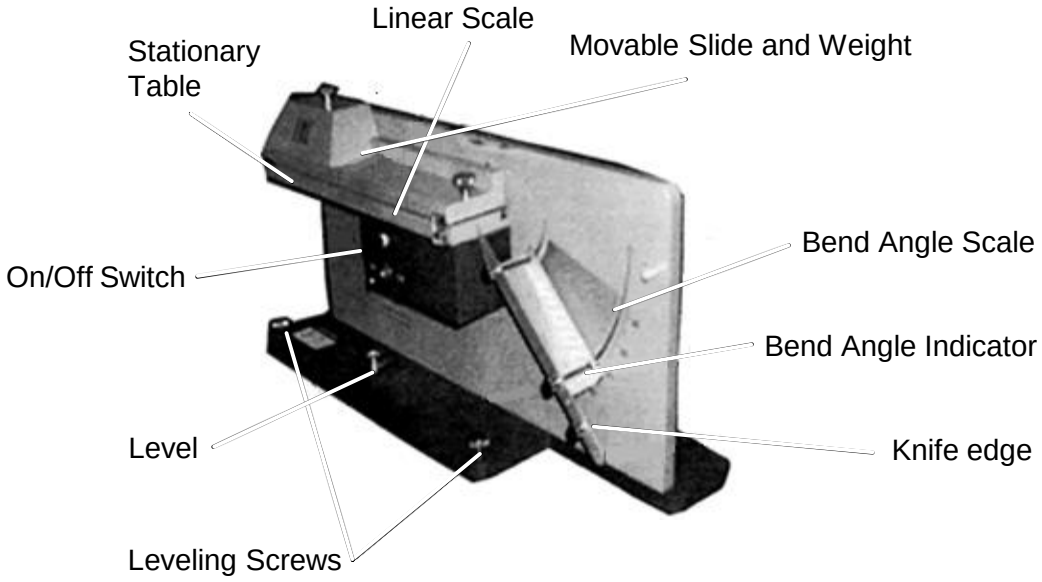


Fig. 2.21: Example of a Motorized Cantilever Test Apparatus [www11c]

The standard ASTM test method D-1388 can be used.

2.6.3 Testing methods for fibers

Knowing the fiber´s elastic modulus (E) and the area moment of inertia (I) of the fiber cross section, it is possible to estimate the fiber´s bending stiffness (E·I). This method can be applied for dry and wet fibers.

Single fiber bending stiffness can either be determined in the wet or the dry state. For the dry state there are two methods:

- Method I:
  For this method we assume the deflected fiber to be a cantilever beam. (Fig. 2.22)

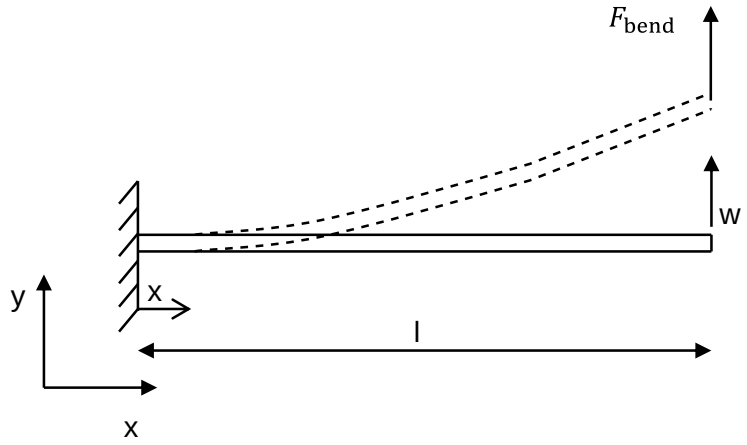


Fig. 2.22: Cantilever beam [WCM14]

By pulling upwards the vertical fiber and deflecting the horizontal one, the bending stiffness of the horizontal fiber is determined. [WCM14]

The fiber-fiber joint configuration is illustrated in Fig. 2.23.

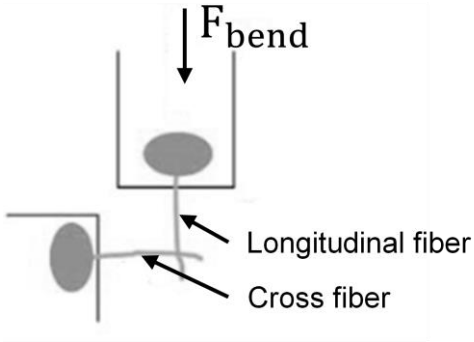


Fig. 2.23: Determination of fiber bending stiffness [WAU14]

- Method II:

  The principle of a beam fixed at both ends is used in this case. (Fig. 2.24)

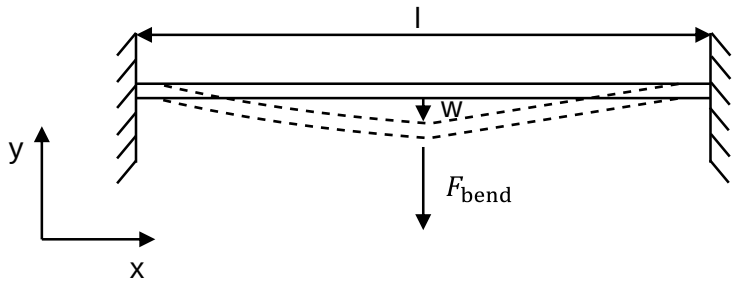


Fig. 2.24: Beam fixed at both ends [WCM14]

Here the longitudinal fiber is replaced by a hook which is used to deflect the cross fiber.

Through the testing procedure and the resulting images of the test, the fiber length (l) and the deflection (w) are measured, as well as the bending force (F_{bend}) using a load cell. With these parameters, the bending stiffness (E x I) of the deflected fiber is calculated using the equation 5 for the method-I and the equation 6 for the method-II: [WCM14]

$$\mathrm{E} \cdot \mathrm{I} = \frac{\mathrm{Fbend} \cdot \mathrm{l}^3}{3 \cdot \mathrm{w}} \tag{2.5}$$

$$\mathrm{E} \cdot \mathrm{I} = \frac{\mathrm{Fbend} \cdot \mathrm{l}^3}{192 \cdot \mathrm{w}} \tag{2.6}$$

Where E is the modulus of elasticity (or Young's modulus, a property of the material), and I is the moment of inertia (based on the geometry of the beam).

2.6.4 Testing methods for drug-eluting stents (DES)

Bending stiffness is influenced by the ratio of the bending force and the deflection of the stent delivery system (SDS) due to this force. Therefore, the larger the ratio, the higher is the bending stiffness. To determine the ratio between force and deflection, the setup of the experiment creates a deflection (f) for a free bending length (l), and measures the resulting force F with a load cell. [WPL14]

The bending stiffness is calculated taking the value of F/f calculated by linear regression from the whole force-distance curve through the following equation:

$$\mathrm{E} \cdot \mathrm{I} = \frac{\mathrm{F} \cdot \mathrm{l}^3}{3 \cdot \mathrm{f}} \tag{2.7}$$

Bending stiffness is measured and averaged in five directions around the circumference due to possible asymmetric structures of the test samples. Fig. 2.25 shows the experimental setup to measure bending stiffness. [WPL14]

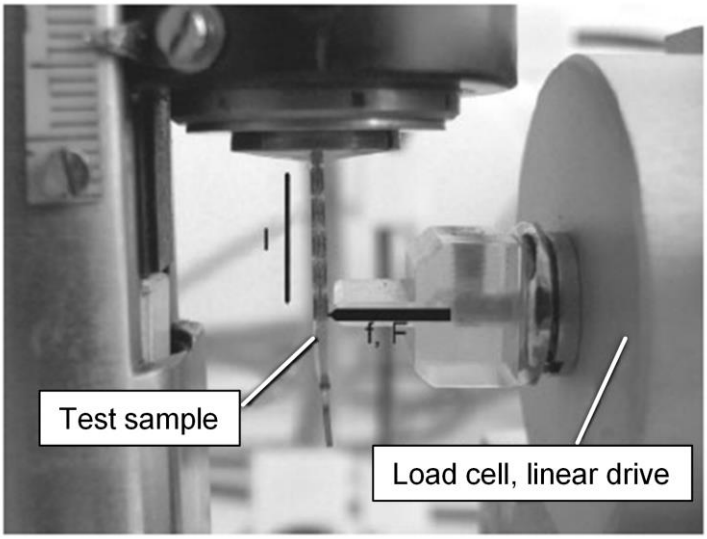


Fig. 2.25: Experimental setup [WPL14]

Another method for testing the bending stiffness of a DES is the three point test method.

In this test, in order to measure the stent bending, a constant moment without radial deformation is applied to the specimen. For this, both ends of the stent are attached to acryl resins bars before the bending measurement.

The deforming force only affects the stent, due to the fact that the acryl resins bars possess a much higher bending stiffness (1.76×10^5 N · mm^2). Denominating the displacement of the contact points C or D as U (Fig. 2.26), the bars make an angle (α). This relation is represented in the equation 2.8: [KMT05]

$$\alpha = \tan^{-1} U / (L/3) \qquad (2.8)$$

By means of the constant moment M and the angle between both ends of the beam α, the bending stiffness EI can be calculated using the following equation: [KMT05]

$$E \cdot I = M \cdot L_{stent} / 2a \qquad (2.9)$$

Where L_{stent} is the length of the stent and the deflection y_{max} is represented by the equation 2.10:

$$y_{max} = a \cdot L_{stent} / 4 \qquad (2.10)$$

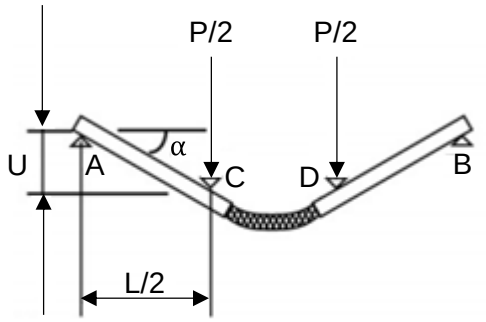


Fig. 2.26: Schematic of the bent specimen distribution [KMT05]

3 Methods and materials

Through the testing of the process parameters with different methods such as one-factor-at-a-time and factorial design, it is possible to check the effects of each value on the process and in the final fiber. The main parameters that are needed to be tested are: draw ratio and speed of the spinning pump since these two parameters have the greatest influence on the diameter and tenacity of the fiber. By varying these parameters, it will be investigated whether an adequate flexural strength, bending stiffness and the required final diameter can be achieved.

By changing the spinning pump velocity, the volume flow of polymer can increase, which means that according to the conservation of mass, the higher the volume flow, the easier it will be to achieve a bigger final diameter. The draw ratio is the parameter that defines the final tenacity, bending stiffness and diameter. Good final mechanical properties are needed in order to be able to manufacture a proper stent, so the main effort of the present thesis will be to achieve a draw ratio as high as possible to get a fiber with the right properties and dimensions.

3.1 Preliminary test

Before starting changing all the parameters to achieve the right mechanical properties, a preliminary test is carried out on the machine. As explained in the previous section, the spinning pump velocity is important for the experiment since it affects the stability of the process.

For high velocities, the process might not be stable so the first thing needed to control the process is to vary this parameter.

In order to get the spinning pump speed maximum value, it is necessary to test a lot of values, starting with a low one and finishing with the highest possible. So the point of the test is to check how the ascending values affect the process to choose the most suitable one. For this, the method called “one factor at a time” is carried out. It is a method of designing experiments involving the testing parameters one at a time, instead of multiple parameters simultaneously. This method system is shown in Fig. 3.1.

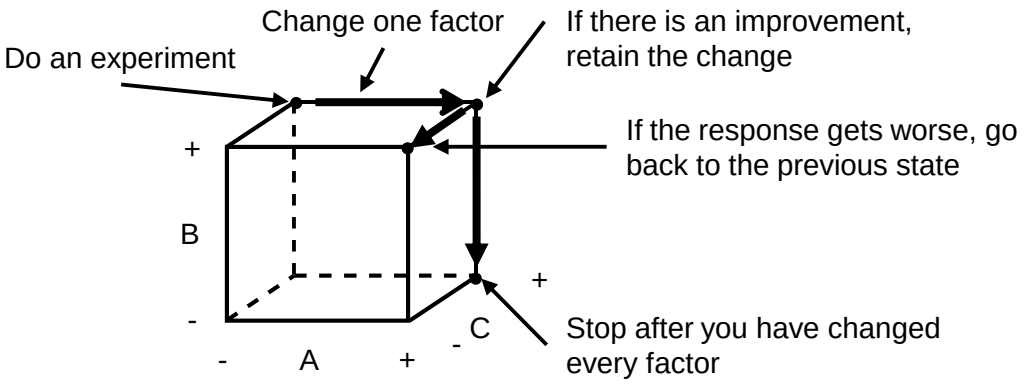


Fig. 3.1: One factor at a time method [CRD14]

Therefore, the preliminary test consists of gradually increasing the speed of the spinning pump until reaching the maximum speed that allows the process to be stable. By this way, the volume flow will be the maximum possible and bigger diameters could be obtained. Once the maximum speed is known, the rest of the experiment is performed with this value of the pump speed and polymer volumetric flow rate.

3.2 Factorial design

In order to see and determine the effects of the parameters which will be varied (explained in 3.3), a factorial design experiment is performed. Factorial designs are a form of simple and efficient experiment, where multiple factors are manipulated or allowed to vary.

When using a factorial design, the independent variable is referred to as a *factor* and the different values of a factor are referred to as *level.* [Pau18]

In factorial design, the levels of two or more independent variables are crossed to create the study conditions. An interaction between these factors is defined as the effects of one variable vary according to the levels of another variable. In order to detect these interactions, it is necessary to examine the variables in combination. [Pau18]

There are three main advantages:

1. They allow researchers to examine the main effects of two or more individual independent variables simultaneously.
2. They allow researchers to detect interactions among variables.
3. Because of this crossed design, factorial design enable researches to examine the effects of the independent variable on a dependent one.

Therefore, with this experimental method, the parameters of the spinning process such as the speed of the godets or its temperature, will be analyzed in order to see their effects

and choose the most suitable value for the final characteristics of the fibers of each parameter.

3.3 Parameters

The end-user properties of PP mainly depend on the degree of crystallinity as determined by the processing conditions. [HJP14]

On the one hand, in order to have a strong influence on the tenacity, the degree of fiber orientation is controlled by the quenching conditions and drawing ratio. As mentioned in section 2.3, the orientation of the polymer chains that form the fibers and the degree of crystallinity has a great influence on the mechanical characteristics of the yarn. Therefore, a wide range of orientation and crystallinity may be obtained by an appropriate selection of the extrusion and drawing conditions. [HJP14]

On the other hand, the final properties of a monofilament such as tensile strength, elastic modulus, and bending stiffness are determined by the spinning process.

The first parameters that affect the process are those which are related to the extrusion conditions: pressure and spinning pump velocity. Both should be constant to ensure the stability of the spinning process. Regarding the spinning pump velocity, the preliminary test explained in section 3.2 is performed first and then this value must be constant. Despite the increase of the pump speed, the pressure remains constant. If that speed increases, the extrusion velocity increases too, which means that the pressure does not change. After extrusion, the monofilaments pass through the cooling chamber, which temperature should be also constant throughout the process.

The draw ratio is the most important parameter to change in order to achieve good mechanical properties.

First, the elastic modulus is the measure of rigidity or stiffness of a material, and it is determined as the slope of the stress-strain curve in the linear proportionality range (Fig. 2.8). It also mainly improves increasing the draw ratios. [HJP14]

Tenacity of monofilaments is another parameter to evaluate. There is a tendency that the tenacity increases as the drawing ratio in the drawing zone becomes higher.

Therefore, the higher the draw ratio, the higher the crystallinity, tenacity and elastic modulus of PP monofilaments. This relation between the draw ratio and the crystallinity of the fibers is shown in Fig. 3.2. However, if the ratio increases, the cross-sectional area will decrease.

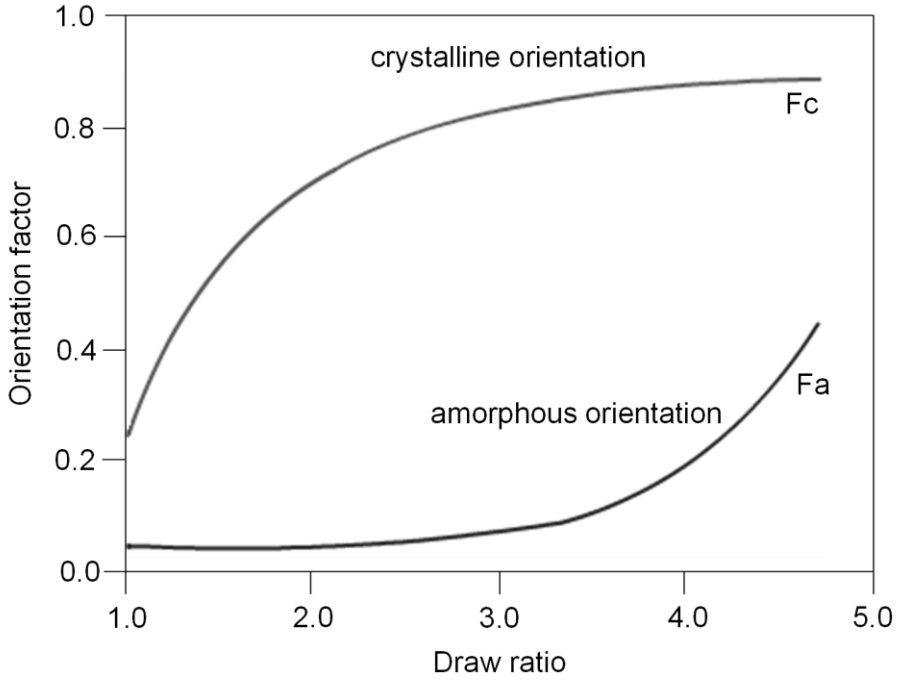


Fig. 3.2: Crystalline and amorphous orientation factors fc and fa of drawn yarns as a function of draw ratio [www19d]

Apart from the draw ratio, cooling and quenching temperatures affect the mechanical properties too. Depending on the quenching speed and the cooling temperature of the filaments, one microstructure or another will form in the fiber. On the one hand, fast quenching leads to amorphous filaments with a large number of small crystallinities, because the growth of the crystal is retarded. This type of filament exhibits toughness and flexibility.

On the other hand, if the cooling bath temperature is high, the final filament will become more crystalline and exhibit superior strength and rigidity, as the increase in cooling temperature promotes crystal growth. [HJP14]. Moreover, an increase in the drawing temperature resulted in decreased shrinkage. [Twa12]

Speed is also an important parameter in the spinning process and has an effect on the process output. The fiber structure and consequently the physical-mechanical properties of the filaments are largely influenced by the spinning and drawing speeds. If the speed increases, the fiber orientation will increase too, so properties such as tenacity or elastic modulus will improve. [Twa12]

3.4 Analytical methods

In this section, the methods of analysis for characterizing the structure and mechanical properties and orientation are explained.

3.4.1 Surface structure

The diameter and the cross sectional properties of the resulting fiber are essential to achieve high bending stiffness. For that, the analysis is divided in two parts. In the first one, the fiber digitized and in the second, the obtained images of the fiber cross section are analysed.

For this purpose, it is needed an instrument to measure the diameter and check that its value is the right one. An optical microscopy (OM) will be used for that purpose. This type of microscopy is characterized by using a system of lenses to magnify images of small objects through light.

3.4.2 Mechanical properties and tensile test

As explained throughout the thesis, mechanical properties and diameter of the fiber are the two main targets of the manufacturing of the fiber.

Due to the fact that bending stiffness is the main property to be observed, the test methods explained in section 2.6 will be used to measure this property. Moreover, it is necessary to measure properties such as Young´s modulus and the elongation at break.

To determine tensile strength, a uniaxial test is performed. For that, individual fibers are loaded to failure. Once the testing procedure is over, the exact initial fiber length (l_0) and the length directly before braking (l_1) are determined. These length values are used to calculate the elongation of the tested fiber according to the next equation:

$$\varepsilon = \frac{\Delta l}{l_0} = \frac{l_1 - l_0}{l_0} \tag{3.1}$$

The results of the single fiber tensile test (F_{break}, strain to failure ε), in combination with the cross sectional area (A_{cross}) obtained for the surface structure analysis, are used to calculate the E modulus through the following equations:

$$\sigma = \frac{F_{break}}{A_{cross}} \tag{3.2}$$

$$E = \frac{\sigma}{\varepsilon} \tag{3.3}$$

The tensile test to be carried out is regulated by some parameters.

First, it is needed to choose the type of test correctly. In this case, it will be a test with constant speed. In addition, a preload is carried out to ensure the correct clamping of the fiber and so that the force system is in a static position. The initial tension will be 0.5 cN/tex. [www05]

There are many options to indicate the end of the test, such as time or when there is a certain percentage of the drop of force. In this test, the indicator will be the last option, in such a way that tensile strength and elongation at break are measured to a 50% decrease in force. [www05]

The applied loads shall be measured with the help of a load cell. In this case, the type of load cell is 100 N for the yarns of the small machine and 10 N for the ones of the large one. To measure materials that bear less effort or to test films or reduced thicknesses, lower loads should be used. The applied gauge length will be 50 mm, as well as the tensile velocity will be 50 mm/min. [www05]

Once the tensile test is finished, with the resulting stress-strain curve it is possible to observe the fiber mechanical characterization comparing the resulting curve with Fig. 3.3.

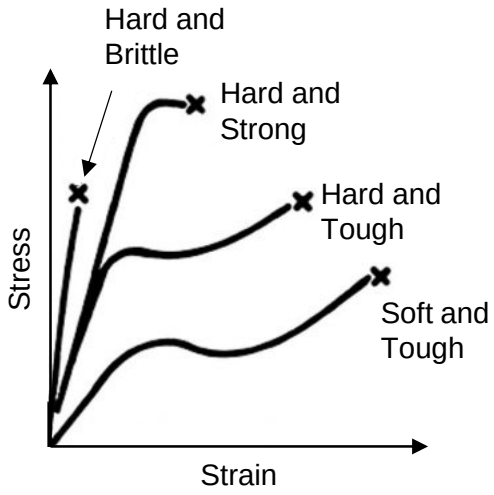


Fig. 3.3: Types of fiber stress-strain curves [www17b]

3.4.3 Yarn count

The yarn count is a numerical expression which defines its fineness or coarseness. It also expresses weather the yarn is thick or thin. Therefore, count is a number which indicates the mass per unit length or the length per unit mass of yarn. [www13c]

In order to measure this number, there are three main unit system: denier, tex and decitex.

- Denier: It is defined as the weight in grams of 9000 m.

$$\text{Denier} = \frac{1\ \text{g}}{9000\ \text{m}} \tag{3.4}$$

- Tex: It is defined as the weight in grams of 1000 m.

$$\text{Tex} = \frac{1\ \text{g}}{1000\ \text{m}} \tag{3.5}$$

- Decitex (dtex): It is defined as the weight in grams of 10000 m.

$$\text{Decitex} = \frac{1\ \text{g}}{10000\ \text{m}} \tag{3.6}$$

Due to the fact that the final diameter of the fiber is one of the requirements in this thesis, it is important to know the relation between the diameter in micrometres (μm) and the yarn count in one of these unit systems. This relation is shown in equation 3.7:

$$\emptyset(\mu\text{m}) = \sqrt{\frac{4 \cdot 10^2 \cdot \text{dtex}}{\pi \cdot \rho}} \tag{3.7}$$

3.5 Material

The material used in this work is polypropylene (PP) in granules. Polypropylene is a linear hydrocarbon polymer (expressed as C_nH_{2n}) and a saturated polymer. Moreover, is one of those most versatile polymers available with applications, both as a plastic and as a fiber. [www13b]

As explained in section 2.2, PP is the best option for the manufacture of monofilaments and medical applications, due to its versatility. The reason why PP is so versatile is because of its properties: [www13b]

- Good chemical and heat resistance
- Toughness and elasticity
- Good fatigue resistance
- Translucency
- Semi-rigidity
- Does not present stress-cracking problems

On the other hand, polypropylene presents important characteristics, which are shown in Table 3.1.

Tab. 3.1: Polypropylene properties [www14b]

Physical Properties	Value
Tensile Strength	0.95 - 1.30 N/mm^2
Thermal coefficient of expansion	100 - 150 x 10^{-6}
Melting point	160 ºC
Density	0.905 g/cm^3, amorphous 0.855 g/cm^3, crystalline

Through the volume of the pump and the velocity of the spinning pump it is possible to calculate the required volume flow of polypropylene with the following equation:

$$V_{pump} \times \omega = Vp \tag{3.8}$$

4 Experimental

The melt spinning setup used in this thesis consist of an extruder, a metering pump, a spin pack, a cooling chamber, three pairs of heated godets and a winder. The experiments will be performed in ITA laboratories and two melt spinning machines will be used. In the small one, called “KSE”, a water bath will be used as a cooling method for the monofilaments, while in the large one, called “Kl. Bicomponent”, the cooling and solidification of the fibers will be carried out by means of an air chamber.

4.1 Process schematic

The process schematic of the big and small machine is shown in Fig. 4.1 and Fig. 4.2 respectively.

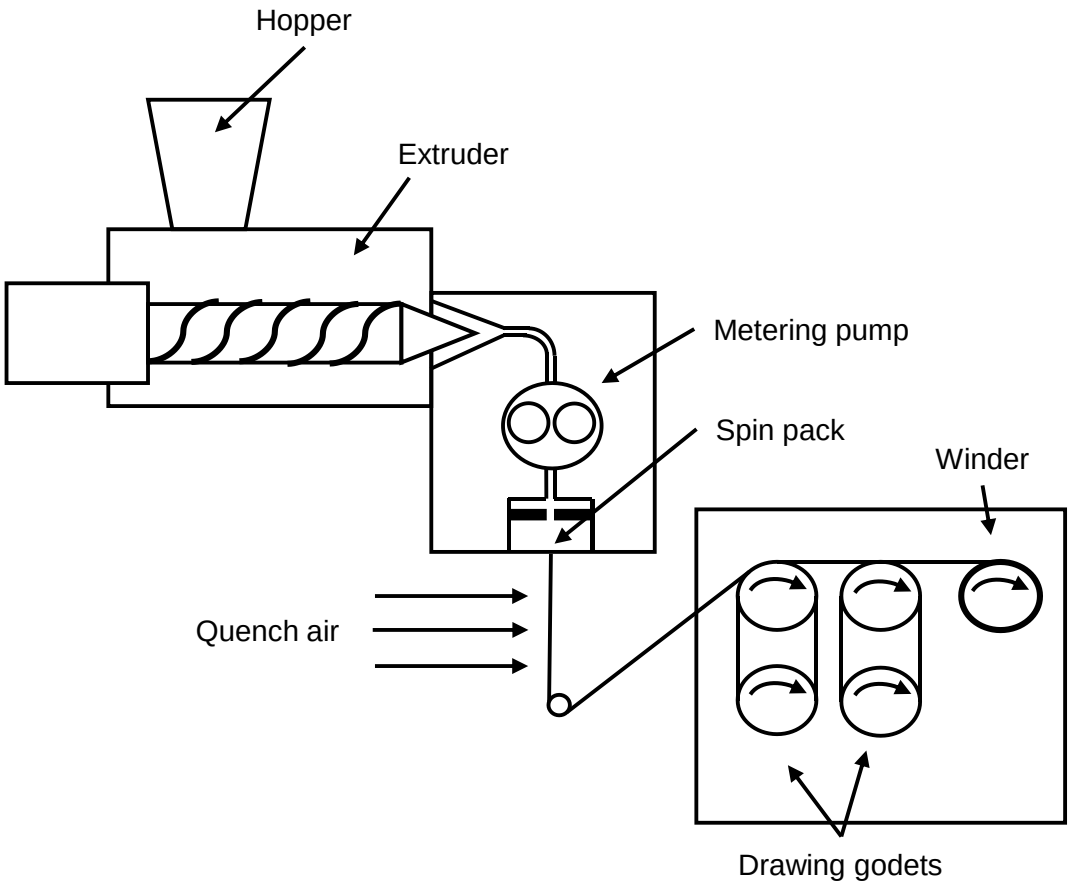


Fig. 4.1: Melt spinning process schematic of the Bicomponent machine

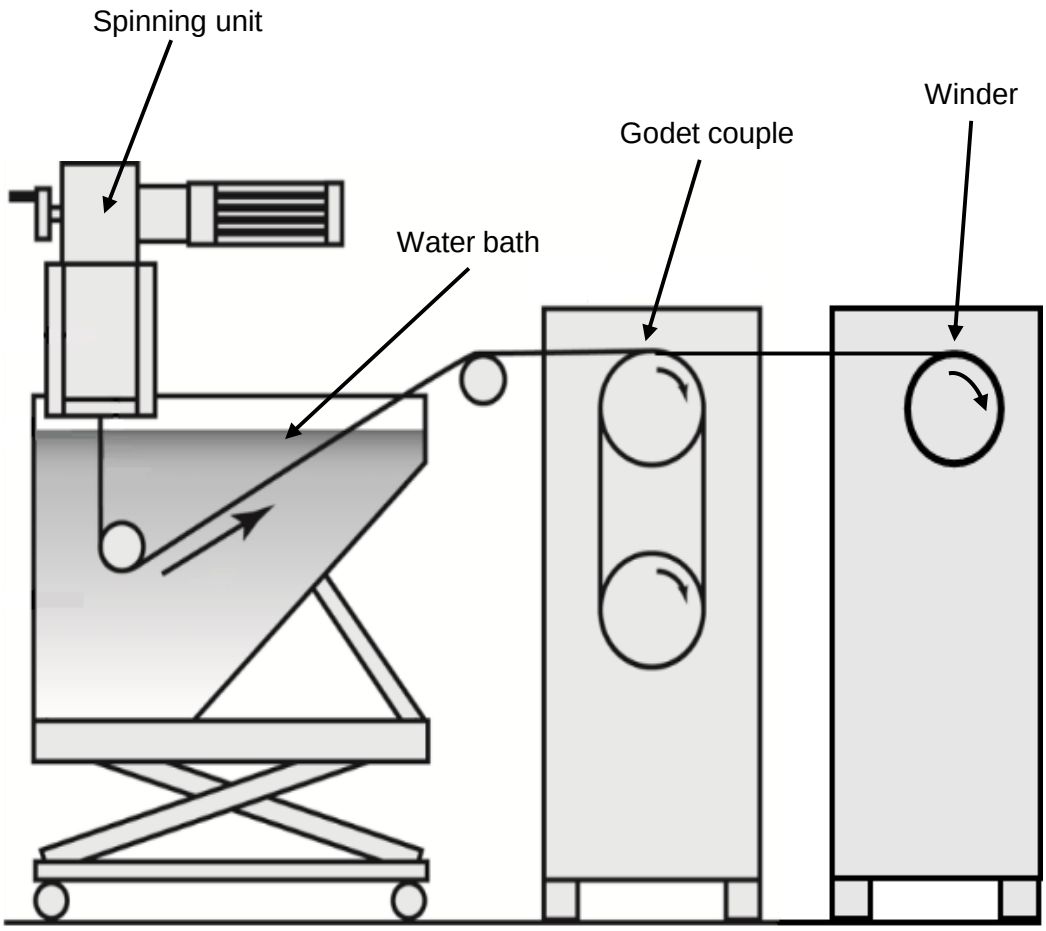


Fig. 4.2: Melt spinning process schematic of the KSE machine [HAL15]

4.2 Parts of the process

4.2.1 Extruder

As explained briefly in section 2.3, the extruder has multiple functions. First, it extracts the material in granules from the feed system and leads it to the time it compresses it to remove trapped gases. Second, it mixes and produces a homogeneous melt to ensure continuous spinning without any breaks or non-uniformity in the spun yarns and finally provides sufficient pressure to overcome the flow resistance so that the flow reaches the metering pump. [www19d]

The functional parts of an extruder are shown in Fig. 4.3. The extruder is basically formed by a cylindrical body within which close-fitting screws rotates. The raw material in the form of granules passes through a hopper that constantly supplies the heated cylinder, inside of which is a screw. This screw pushes the material along the cylinder and at the

same time generates pressure and mechanical shear in the polymer, which further increases the temperature to melt and homogenize the material. Finally, when the molten polymer reaches the end of the screw, it is guided to a gear pump which regulates the volume of polymer desired to reach the spin pack. Screws with a diameter of 45 - 300 mm are used for polypropylene with a melting capacity of 50 - 2000 kg/h. [VGK97]

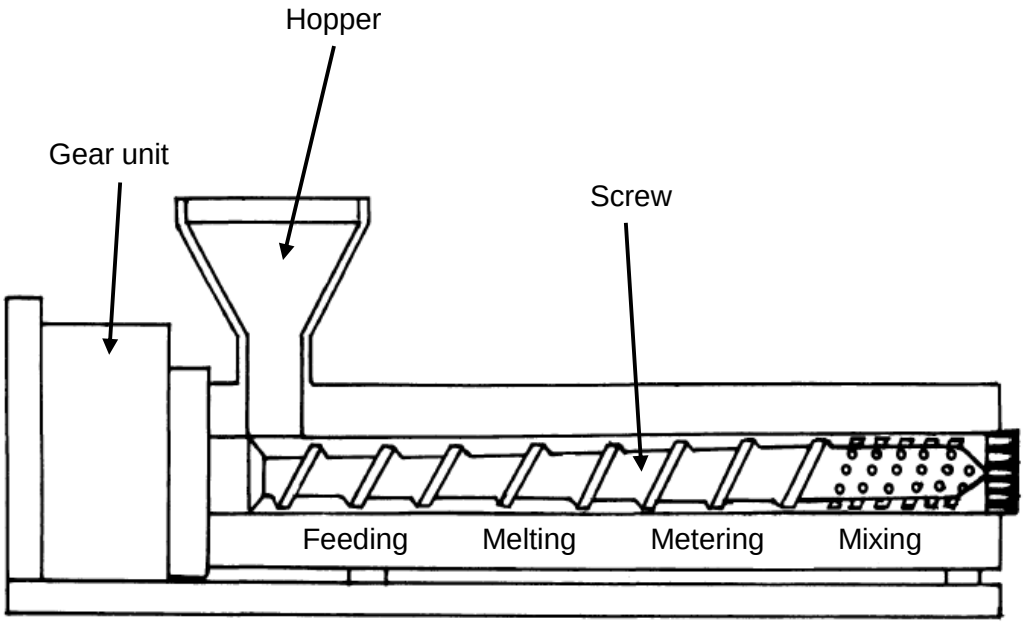


Fig. 4.3: Functional parts of an extruder [VGK97]

4.2.2 Metering pump and spin pack

It is common to install a gear pump between the extruder and the spin pack to provide uniform pressure and flow through the spinneret. Any pressure or throughput variation changes the filament diameter, which affects both processing and product quality. The metering pump mainly consists of two gear wheels (Fig 4.4), and reduce any output variation from the extruder, as well as regulate the molten polymer flow. [www19d]

Through the metering pump, the constant molten stream is transported under pressure to spinning heads. In this part, a measured amount of molten polymer is conveyed to the spin pack, which is reached through a hole in the spinning heads. [VGK97]

The transport of the melt is carried out in the following way: the gear teeth of both wheels open opposing spaces when turning. The polymer enters from the one side coming from the feed channel and fills the empty spaces between the two teeth of each gear. When the two wheels rotate, they push the melt into the spin pack. [VGK97]

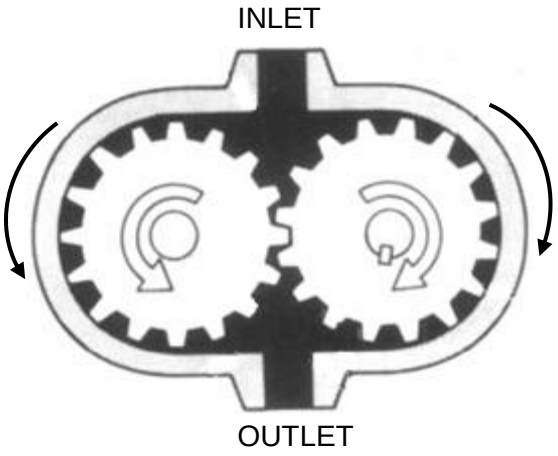


Fig. 4.4: Metering pump gears [Hau97]

The pump regulates the flow of polymer through the equation 3.8. It has a constant volume, so by varying the speed, different polymer flow volumes can be achieved.

The parts of a spin pack are shown in Fig. 4.5. The most important part is the spinneret, the role of which is to impart cross-sectional shape to the extruded filaments. There are also another parts such as the melt reservoir and filter that removes the solid particles of the melt avoiding a block of the spinneret hole and the gaskets, which are mechanical seals filling the space of two contact surfaces whose function is to prevent the entry and emissions of both liquids and gases when applying intense pressures and temperatures. [www18e]

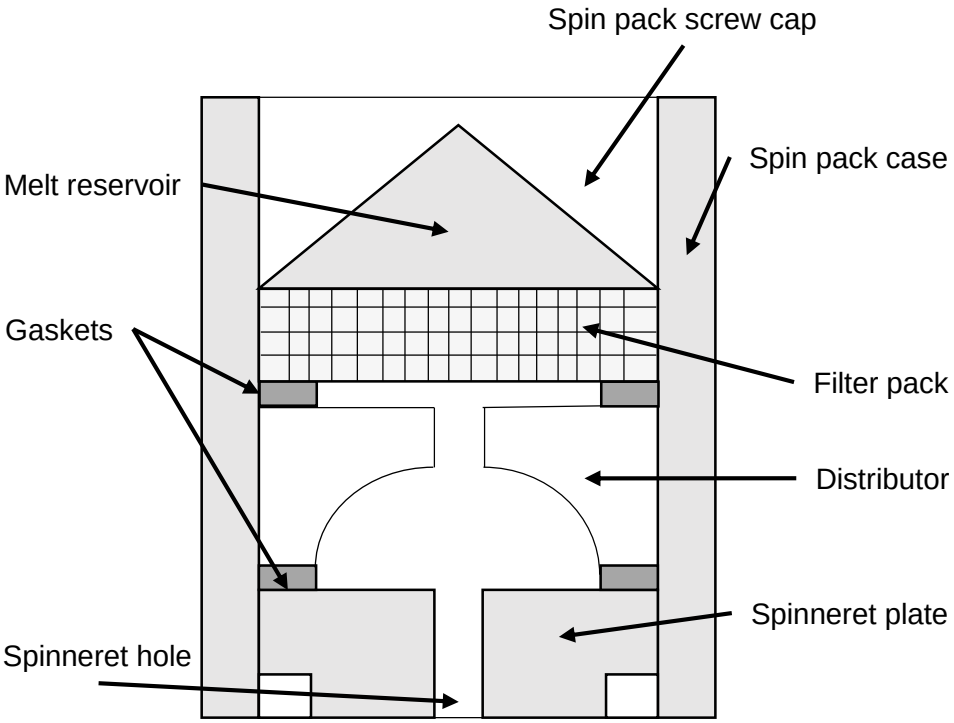


Fig. 4.5: Spin pack scheme [www19d]

In the following picture (Fig. 4.6), the extruder and spin pack of the small machine at ITA are shown.

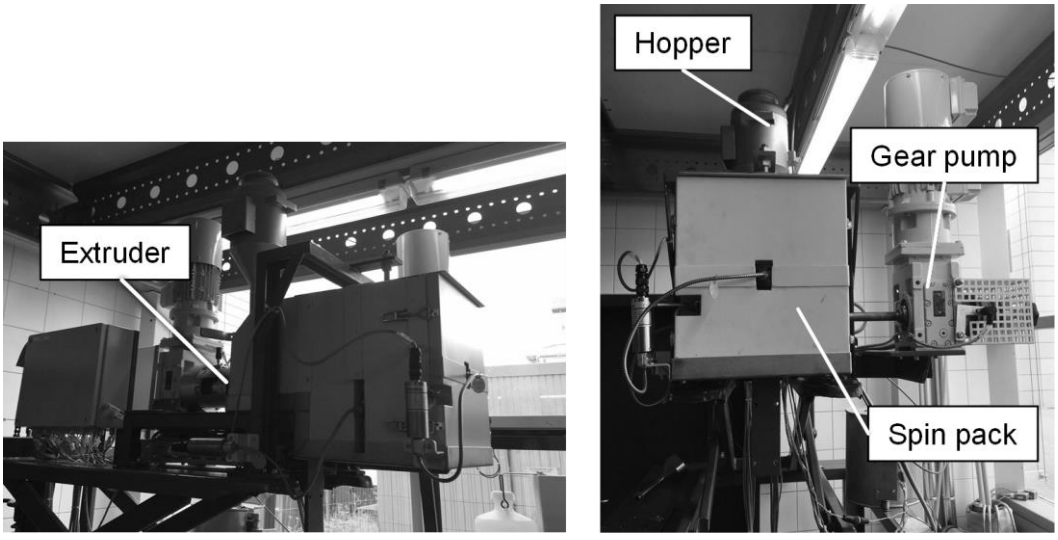


Fig. 4.6: Image of the spin pack and extruder

4.2.3 Cooling system

The cooling system is the part of the spinning process where the fibers are cooled and solidified. There are two main methods of cooling: with air (through an air chamber) for

the big machine and with water (with a water bath) for the small one. Although for monofilaments is better to use a water bath (bigger diameters) since the cooling is faster due to increased heat transfer, both methods will be performed.

The water bath is under controlled and constant temperature and induces phase separation and solidification of the fiber extruded by means of polymer crystallization [KMo14]. The water bath used in ITA's laboratory is the one shown in Fig. 4.7.

For the air method, there are three quenching systems: cross-flow, in-flow and out-flow quench. Cross-flow quench is used for fine and large deniers and for round and rectangular spin packs. Therefore, it will be the air quenching system used in this thesis. In contrast, in-flow quench is used in spinnerets where the filaments are arranged in a ring shape, and out-flow is used for larger spinneret diameters. [VGK97]

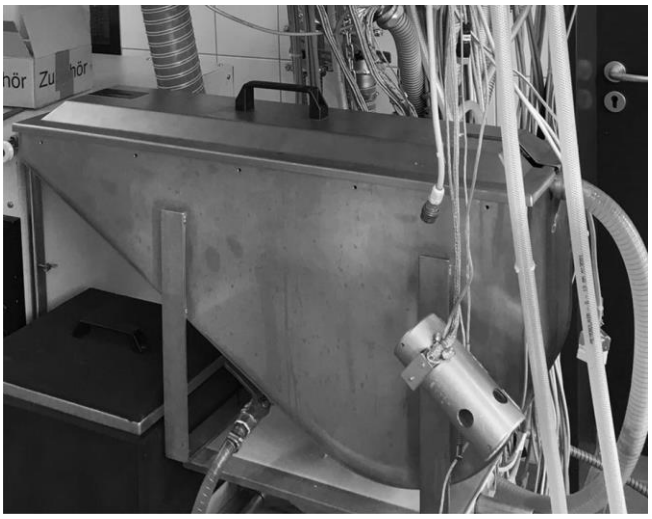


Fig. 4.7: Picture of the water bath

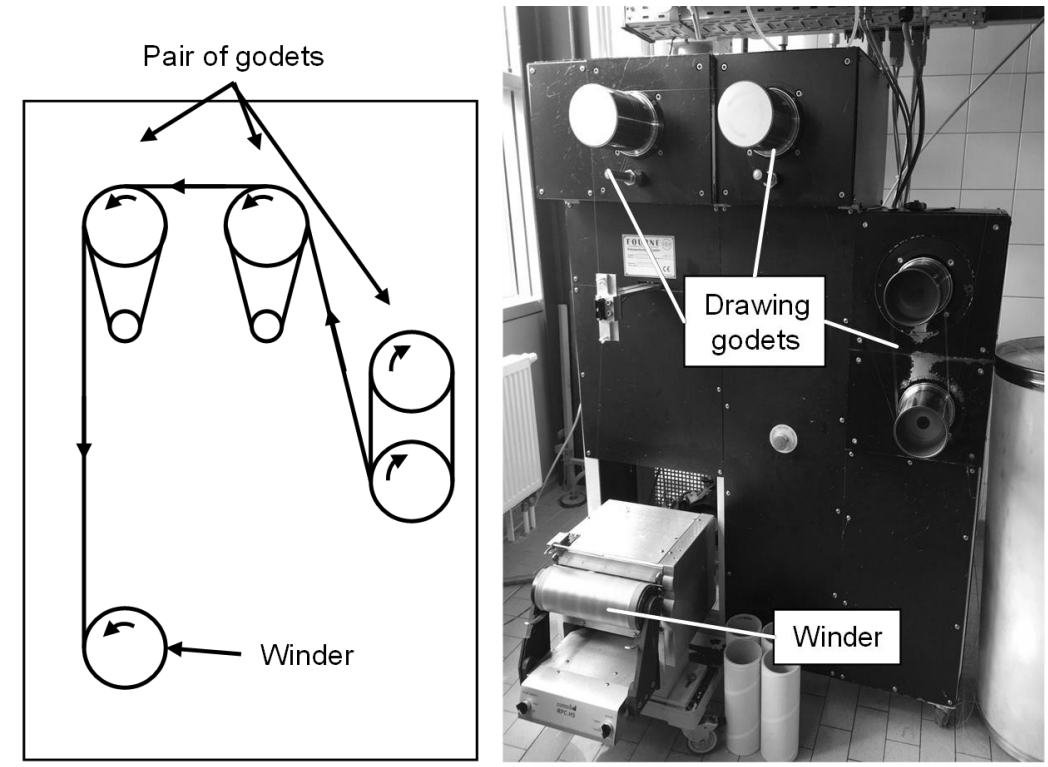
4.2.4 Drawing system and winder

The drawing process is a post-spinning operation for a melt-spun fiber. Normally, after the fibers have solidified, the filaments can be drawn to impart strength and resistance. When drawing, the molecular chains come together and orient along the fiber axis, creating a considerably stronger yarn. Drawing also induces changes in crystallinity levels. As explained in Section 3.3, the draw ratio is closely related with the degree of orientation and crystallinity such that an increase of the draw ratio leads to an improvement in the fiber orientation, resulting in a structure which has much higher strength, elastic modulus, and dimensional stability compared with its undrawn state. [Sen97]

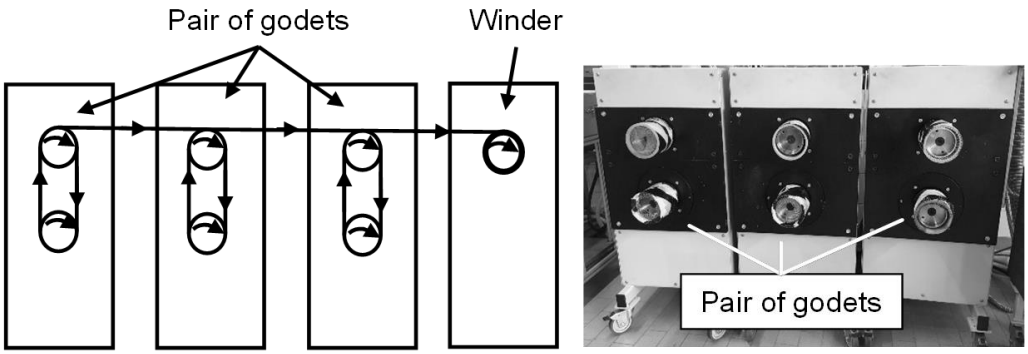
The last part of the process is formed by a winder, where the resulting fibers are coiled. The take-up device or winder is located horizontally below the appropriate spinneret. To

achieve a uniform speed, the tube roller is driven by friction through another roller, which ensures a constant pick-up speed. In order for the filament to fit satisfactory around the bobbin, it is grasped by the forked thread guide and moved equally to the left and the right by means of a traverse guide. [VGK97]

In Fig. 4.8, the pictures of the drawing system and winder of ITA´s machines are shown.



a)



b)

Fig. 4.8: a) Drawing godets and winder of the big machine (process schematic on the left, real image on the right), b) Drawing godets of the small machine (process schematic on the left, real image on the right)

5 Results and discussion

5.1 KSE machine

The first step was to perform an experiment on the small machine in order to get conclusions and parameters for the large one. The set-up shown Fig. 4.2 is the one used for the performance of this experiment.

5.1.1 Preliminary test

In this experiment, a water bath is used as the cooling system of the process. This allows the process to cool the fibers faster than with air and a higher volume flow can be achieved. Thus, the first step of the experiment is to perform a preliminary test in order to gain experience concerning the mechanism of the process and try to define some parameters, such as draw ratio or the spinning pump speed for a possible future adaptation in another machine. Moreover, as it will be performed in the preliminary test of the large machine, the definition of the spinning pump speed will be necessary for the stability of the process and the experiment.

After testing with some increasing values, using the one-factor-at-a-time method explained in section 3.1, the spinning pump speed to be used in this experiment will be 15 rpm.

The volumetric flow of the spinning pump can be obtained with equation 3.8:

$$0.16\ cm^3/rot \times 15\ rpm = 2.4\ cm^3/min$$

5.1.2 Parameters

The main objective of this experiment is to obtain the necessary parameters for the manufacture of fibers with a specific diameter, as well as the appropriate mechanical properties. In this way, in a next step, these parameters can be adapted to a larger and more precise machine for the final manufacture of PP fibers.

At the beginning of the experiment, it is necessary to start with the value of the spinning pump speed which has been defined in the previous test, thus ensuring the stability of the process.

Once the value of the spinning pump speed was determined, it was attempted the realization of a process window, to see which range of draw ratio values could be adequate. The result was the following (Fig. 5.1):

- For values of the draw ratio below 10, the resulting fiber had undrawn parts in its morphology.
- For values of the draw ratio above 10, the process was not stable at all, and the fiber breaks.

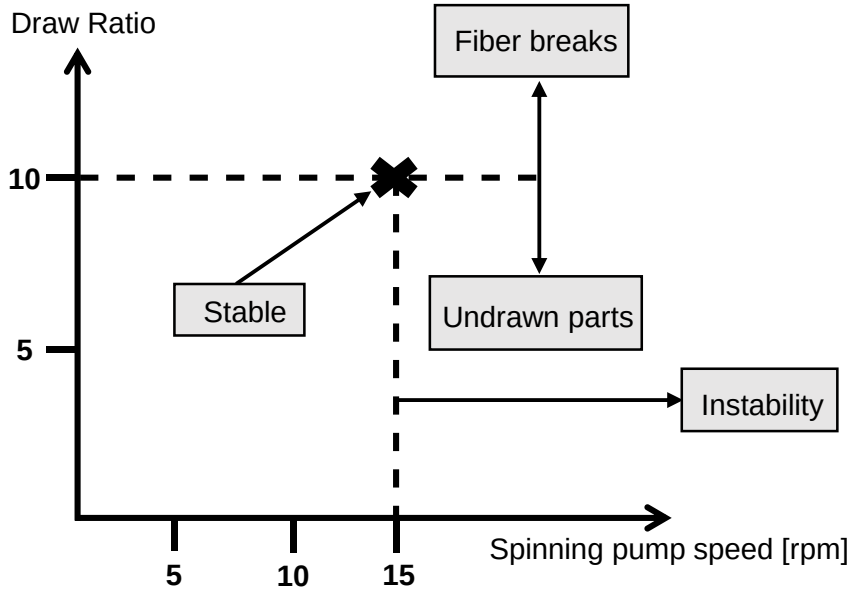


Fig. 5.1: Result of the KSE experiment

Therefore, just for a value of 10 for the draw ratio, the process was both stable and there were no undrawn parts in the fiber. However, due to no obvious reason, the fiber broke after 8 minutes and the process finished.

In order to achieve a high draw ratio (around 10), the following parameters were reached. In this experiment, the godets are unheated, so they are at room temperature, like the water bath (20 ºC)

The final parameters of the experiment are shown in Table 5.1.

Tab. 5.1: Final parameters of the experiment

Parameter	Value
Spinning pump speed	15 rpm
Spinning pump volume	0.16 cm^3/rot
Spinning pump temperature	215 ºC
Spinning head temperature	215 ºC
Water bath temperature	20 ºC
Distance spinneret-water bath	63 cm
First pair of godets speed	9.6 m/min
Second pair of godets speed	96 m/min
Winder speed	90 m/min
Draw ratio	10

5.1.3 Characterization

After the performance of the experiment, it is important to check the properties of the resulting fibers. For that, both the surface of the fiber (diameter and fineness) and the mechanical properties (such as tenacity and bending stiffness) will be tested.

5.1.3.1 Surface morphology

In order to determinate the fineness of the resulting fibers, a fineness test was carried out. The test consists basically in weight a determinate length of the PP monofilament and calculates the fineness in dtex. The fiber was measured three times and the final fineness is the average of the three measures.

The parameters of the test are shown in Tab. 5.2.

Tab. 5.2: Yarn count test parameters

Parameter	Value
Measuring length L	10 m
Temperature	20.7 ºC
Relative humidity	66 %

The results of the test are shown in Tab. 5.3

Tab. 5.3: Yarn count test results

Parameter	Value			
Test nº	1	2	3	Average
Weight	0.3606 g	0.3606 g	0.3701 g	0.3656 g
Fineness	360.57 dtex	366.28 dtex	370.09 dtex	365.65 ± 4.79 dtex

Once the fineness is determined, it is possible to calculate the diameter of the fiber with the equation 3.7, so that it is not necessary the use of an optical microscopy to measure the diameter. The reason why it is necessary to calculate the diameter is because this parameter is one of the most important, since it has a great influence on bending stiffness.

$$\emptyset(\mu m) = \sqrt{\frac{4 \cdot 10^2 \cdot \text{dtex}}{\pi \cdot \rho}}$$

$$\emptyset\ (\mu m) = \sqrt{\frac{4\ \text{x}\ 10^2\ \text{x}\ 365.65\ \text{dtex}}{\pi\ \text{x}\ 0.905\ \frac{\text{g}}{\text{cm}^3}}} = 226.81\ \mu m$$

This measure of the diameter is high, however, it is below the required value, as the aim of the experiment is to reach diameters close to 300 μm.

5.1.3.2 Tensile test and mechanical properties

The stress-strain behavior of the polypropylene monofilament yarns produced in the small melt spinning machine is displayed in Fig. 5.1. In the curve can be observed the nearly-linear behavior before breaking abruptly. Moreover, the fiber breaks at a high tensile strength and at low elongation, so according to Fig 3.4, the fiber has probably high tenacity and therefore, is high-oriented.

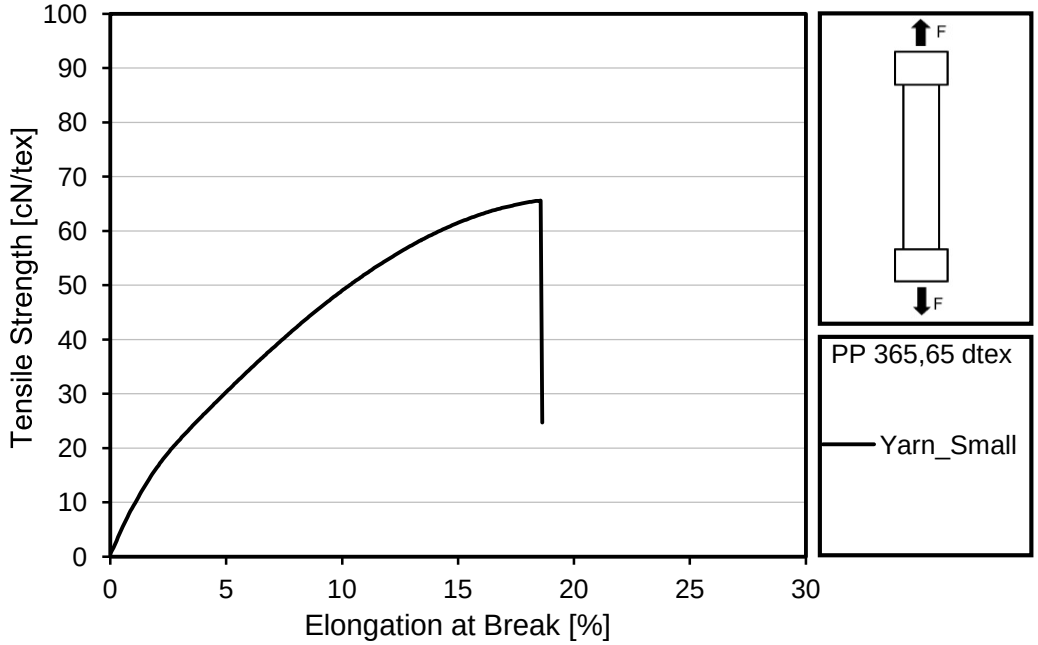


Fig. 5.2: Stress-strain behavior of the yarns produced in the small machine

From this figure many values can be obtained, such as the tensile strength, the elongation at break and due to the fact that the behavior of the material is almost linear, with the equations 3.2 and 3.3 the Young´s modulus E of the fiber can be calculated.

Moreover, the value of the elastic module allows calculating the theoretical bending stiffness of the fiber. Therefore, the value of the moment of inertia of the yarn must be known.

Assuming that the cross-sectional area of the fiber is a perfect circle, the moment of inertia of the fiber can be calculated with the following equation:

$$\mathrm{I} = \frac{\pi \, x \, r^4}{4} \tag{5.1}$$

By this way, and with equation 2.1, the bending stiffness can be calculated. The values of each parameter are shown in Tab. 5.4.

Tab. 5.4: Tensile test results

Parameter	Value
Tensile strength [cN/tex]	65.24 ± 3.74
Elongation at Break ε [%]	18.24 ± 1.43
Elastic Modulus E [MPa]	3236.29
Moment of Inertia I [m^4]	1.3 x 10^{-16}
Cross Sectional Area A_{cross} [mm^2]	0.0404
Bending Stiffness (x10^{-9}) [N·m^2]	420.67

5.1.4 Problems

In spite of having achieved a high draw ratio, as well as a good tenacity, the process gave some problems. First of all, the experiment, once a 10 draw ratio was achieved, did not last more than 8 min. The velocities of the godets and the pump were high and the machine does not work well at high speeds, which means instability and the production of yarns with undrawn parts, as well as different diameters. A reason for that instability and undrawn fibers may be that the spinning machine (extruder, spin pack and metering pump) does not keep the process pressure constant. When there is a variation of the pressure in one of these parts, this change must be followed by the others and compensate the pressure. Moreover, as mentioned before, the extruder does not work properly at high speeds, so when there is an increase in the speed in the drawing system, the extruder did not follow this increase correctly.

5.2 Bicomponent machine

Once the experiments and tests on the small machine are completed, research will continue on the large melt-spinning machine. In the previous section and in the explanation of the experimental set-up in chapter 4, it is seen how for the first experiments on the small machine a water bath is used as the cooling system. However, due to problems of adapting the parameters and devices of the small machine to the large one, an air chamber will be the device in charge of the process of cooling and solidification of the fibers.

5.2.1 Preliminary test

Since it is the first attempt in ITA of production of PP monofilaments with these particular characteristics and measures in this melt spinning machine, a preliminary test is necessary. The operation of the test will be as explained in 3.1, through a one-factor-at-a-time test, the maximum spinning pump velocity that ensures the stability of the process will be tried to be determined. With that value of the spinning pump velocity, and the equation 3.8, the maximum volume flow of polymer is calculated.

The initial parameters for preliminary test are shown in Table 5.3

Tab. 5.5: Initial parameters for preliminary test

Parameter	Value
Spinning pump volume	0.6 cm^3/rot
Spinning pump velocity	15 rpm

Gradually increasing the speed values, it was possible to reach 30 rpm. However, with this value, the process is not as stable as required, which means that adequate pump speed is a value between 25 (the previous stable checked value) and 30.

Now it is possible to calculate with equation 3.8 the maximum volume flow of molten polymer:

$$V_{pump} \times \omega = Vp$$

$$0.6\ cm^3/rot \times 30\ rpm = 18\ cm^3/min$$

$$0.6\ cm^3/rot \times 25\ rpm = 15\ cm^3/min$$

This value of V_p is for a process with an air cooling system, however, if it could be possible to adapt a water bath, both the volume flow and the pump speed will be higher.

The next step is to carry out a process window with the aim of identifying an adequate range for the draw ratio.

5.2.2 Parameters and problems

Once the preliminary test is done and the value of the spinning pump speed has been determined, as well as with the KSE machine, an attempt was made to identify the process window of the experiment, where an adequate range of the draw ratio may be achieved. As explained below, the parameters of the KSE machine could not be adapted to this new experiment, so new parameters had to be calculated.

These parameters are the draw ratio (and consequently the speed of each pair of godets), the winder speed and the temperature of the drawing system. (Section 3.3)

In table 5.6 the initial parameters of the test are shown.

Tab. 5.6: Initial parameters

Parameter	Value
Spinning pump velocity	15 rpm
Air chamber temperature	20 ºC
First pair of godets speed	180 rpm
First pair of godets temperature	20 ºC
Second pair of godets speed	230 rpm
Second pair of godets temperature	120 ºC
Third pair of godets speed	245 rpm
Third pair of godets temperature	110 ºC
Winder speed	250 m/min
Draw ratio	1.36

These values are for a stable process, so now the aim is to achieve better possible mechanical properties through the variation of these parameters.

The draw ratio is the most important parameter to take into account. When increasing the ratio, the polymer chains of the fibers are oriented resulting in a highly oriented fiber, which entails better mechanical properties such as tenacity or Young´s module. To calculate it, the values of each pair of godets speed are necessary. The ratio is calculated with the following equation:

$$\mathrm{DR} = \frac{\mathrm{n_{3p}}}{\mathrm{n_{1p}}} \tag{5.2}$$

Where n_{3p} and n_{1p} is the speed of the third pair of godets and the first one respectively.

In the same way, it is possible to calculate the final diameter of the fiber through a draw ratio and vice versa. For that, knowing the initial diameter of the fiber when it leaves the extruder is necessary according to the following equation:

$$\emptyset\mathrm{f} = \frac{\emptyset\mathrm{i}}{\sqrt{\mathrm{DR}}} \tag{5.3}$$

However, some problems arose while the experiment was taking place.

On the one hand, as said before, a V_{pump} of 30 rpm resulted in problems, since the fibers were not as stable as required when they were in the drawing system.

On the other hand, there was a problem with the winder. As explained in section 4.2.4, the winder is friction-driven by a roller, which ensures the requirement of constant take-up speed. During the experiment, this friction between both rollers did not work and therefore, the winder did not roll up the fibers correctly. Due to this fact, the experiment had to stop, so it was not possible to know experimentally the value of the draw ratio that provides the required final diameter of the fiber, which is about 300 μm, and the process of identifying the process window is not finished. Moreover, a performance of the factorial design method (section 3.2) was supposes to carry out, however, due to these problems it was no possible. The intention of this method was to see and determine the effects of the parameters which were going to be varied, such as the temperature of the godets.

In terms of the fineness (Section 3.4.3), the necessary draw ratio for a specific value of fineness can be calculated. For that, through the density of the material (PP, 0.905 g/cm^3) and the winder speed, the initial mass flow of polymer can be known following the equation 5.4:

$$\rho = \frac{m_p}{V_p} \tag{5.4}$$

$$m_p = 0.905 \ \frac{g}{cm^3} \ \text{x} \ 15 \ \frac{cm^3}{min} = 13.575 \ g/min$$

Once the mass flow is calculated, the next step is to know the final fineness of the yarn taking into account the winder speed (250 m/min):

$$\frac{13.575 \ \frac{g}{min}}{250 \ \frac{m}{min}} \ \text{x} \ 10^3 = 54.3 \ \text{tex}$$

With a value of 25 rpm of spinning pump velocity, a fineness of 54.3 tex (543 dtex) is achieved. This value, linked with the aim of fineness of 300-400 dtex allows to know the maximum draw ratio:

$$DR_{max} = \frac{\frac{543 \ \text{dtex}}{300 \ \text{dtex}} \ \text{x} \ 245 \ \text{rpm}}{180 \ \text{rpm}} = 2.46$$

Where 245 rpm and 180 rpm are the speed of the third and first pair of godets respectively. This result shows that it is possible to increase the draw to 2.46 and the final fiber will still have the required yarn count.

5.2.3 Characterization

5.2.3.1 Surface morphology

The influence of the spinning process parameters on the yarn´s diameter is examined through optical microscopy (OM). Fig. 5.3 and 5.4 show OM of a yarn produced with the setup of the large machine with its diameter measure depending on the used spinning pump velocity for a draw ratio of 1.36.

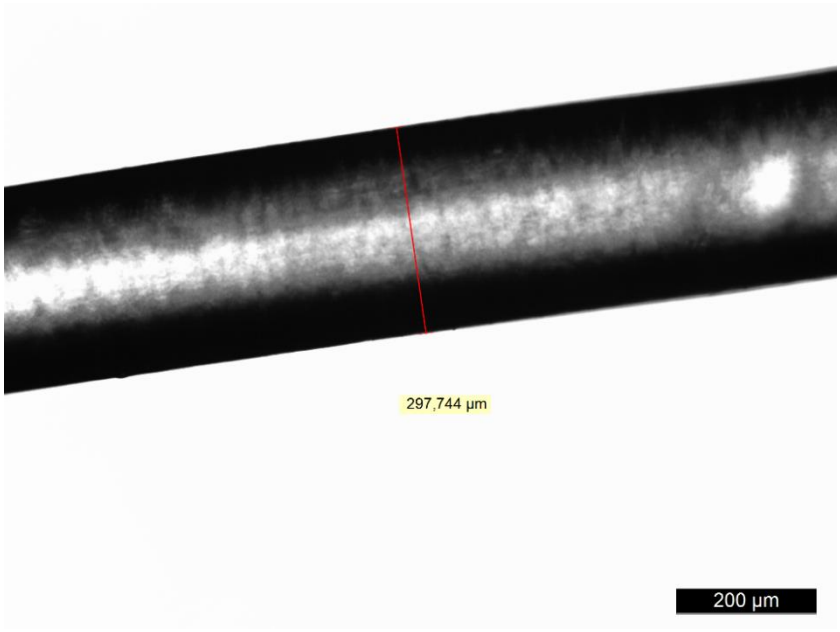


Fig. 5.3: OM image of a yarn produced in the large machine with a spinning pump velocity of 25 rpm

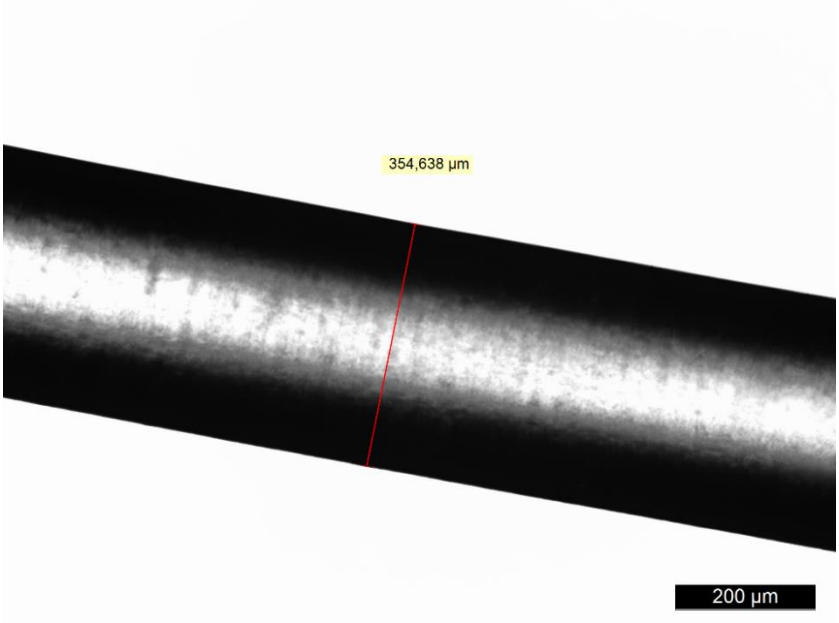


Fig. 5.4: OM image of a yarn produced in the large machine with a spinning pump velocity of 30 rpm

These values of the diameters (297.74 μm and 354.63 μm) show how the conservation of mass is fulfilled, since the higher the volume flow of polymer, the bigger the diameter.

At first, these diameter may seem appropriate, as both are close to or greater than the required value (300 μm). However, the draw ratio is too small, so the mechanical properties of the yarn are probably not the most suitable for the purpose of the thesis.

In order to determinate the yarn count of the different fibers, a fineness test such as the one performed in section 5.1.3.1 was carried out. With the purpose of seeing in a better way the differences between the fibers with different spinning pump velocities, the fiber obtained with a spinning pump speed of 20 rpm was tested, too.

The parameters of the test are the ones which are shown in Tab. 5.2, and in this case also three test were done for each yarn. The results of this test are displayed in Tab. 5.7, where Yarn_20, Yarn_25 and Yarn_30 correspond to the fibers that have been spun at 20, 25 and 30 rpm respectively.

Tab. 5.7: Yarn count test results

Test nº	Yarn_20		Yarn_25		Yarn_30	
	Weight	Fineness	Weight	Fineness	Weight	Fineness
1	0.3718 g	371.84 dtex	0.4958 g	495.77 dtex	0.6055 g	605.53 dtex
2	0.3975 g	397.53 dtex	0.4527 g	452.73 dtex	0.6009 g	600.89 dtex
3	0.3824 g	382.35 dtex	0.4979 g	497.86 dtex	0.5510 g	551.02 dtex
Average	0.3839 g	383.91 ± 12.92 dtex	0.4821 g	482.12 ± 25.47 dtex	0.5858 g	585.81 ± 30.22 dtex

As has been done in the surface morphology section of the small machine, it is possible to calculate the diameter using equation 3.7, so that the difference between the mathematically calculated diameters ($\text{Ø}cal$) and the values obtained with the optical microscopy ($\text{Ø}mic$) are compared in Tab. 5.8. For the calculation of the diameters, the values of the fineness shown in the previous Table are needed.

Tab. 5.8: Comparison between values of fiber diameters

	$\text{Ø}cal$	$\text{Ø}mic$
Yarn_20	232.4 μm	-
Yarn_25	260.9 μm	297.7 μm
Yarn_30	287.05 μm	354.63 μm

Looking at the table, it is seen how, at higher spinning pump speed, both the fineness and the diameter of the fibers are bigger. The values of the diameters calculated and measured with the microscopy are not very similar, being the difference between them very big. The reason for the difference could be that the value of the fineness used is the average value without the standard deviation, so the calculated values are not entirely correct.

5.2.3.2 Tensile test and mechanical properties

The stress-strain behavior of the yarns produced with the large machine is displayed in Fig. 5.5. Although the three behaviors are similar, it is observed how the lower the spinning pump speed, the higher the tensile strength but the smaller the elongation at break, the opposite being the case when the pump speed increases. In the three cases, the linear region is too small, being even difficult to recognize it. According to Fig. 3.4, the three yarns are neither brittle nor hard (thus the fiber is amorphous), as the maximum tensile strength achieved is not so high. In contrast, the achieved elongation at break is very high.

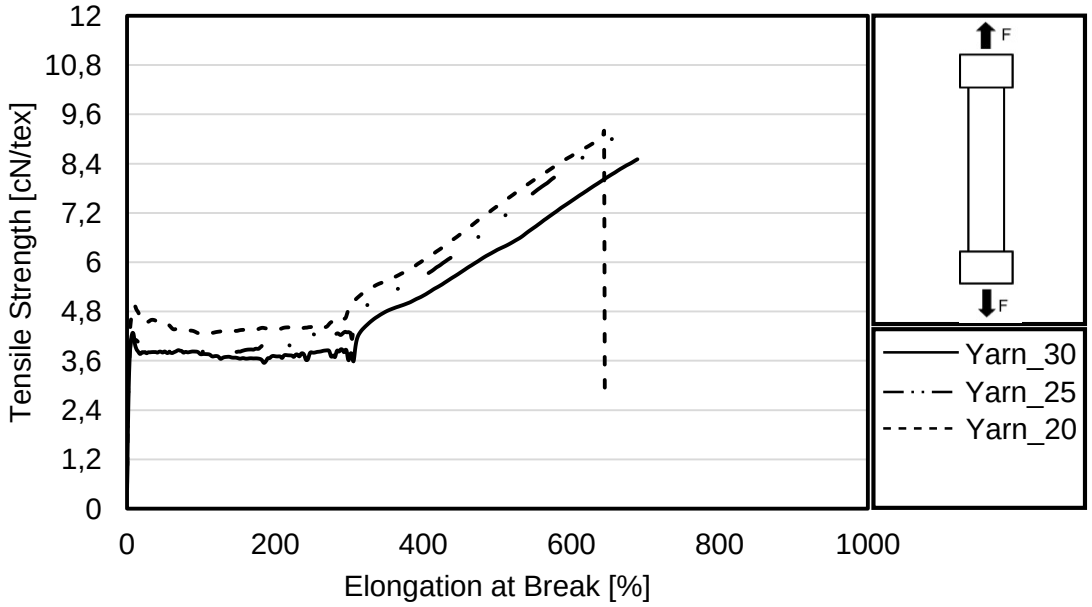


Fig. 5.5: Stress-strain behavior of the yarns produced in the large machine

As mentioned in the other tensile test section (5.1.3.2), some important parameter´s values can be obtained from Fig. 5.5. To the calculation of the values which are not directly in the figure, the equations 3.2, 3.3, 2.1 and 5.1 were used. These values are shown in Tab. 5.9.

Tab. 5.9: Results of tensile test

Parameter	Value		
	Yarn_20	Yarn_25	Yarn_30
Tensile strength [cN/tex]	9.2 ± 0.68	9.02 ± 0.97	8.5 ± 1.06
Elongation at Break ε [%]	645.89 ± 169.06	658.96 ± 153.7	688.38 ± 209.79
Elastic Modulus E [MPa]	12.18	9.48	7.31
Moment of Inertia I [m^4]	1.6×10^{-16}	3.85×10^{-16}	7.76×10^{-16}
Cross-Sectional Area A_{cross} [mm^2]	0.0448	0.0646	0.0987
Bending Stiffness [$N \cdot m^2$]	-	-	-

Regarding the tensile strength, the values of the three fibers are not very high, and they are so much lower than the tensile strength achieved in the other experiment. This is normal since the draw ratio is also lower than the one reached in the small machine.

The calculation of the bending stiffness for these fibers is not possible. The value of the Young´s Modulus of each fiber is necessary (Equation 2.1) and for that, the linear regime of the stress-strain curve of each fiber is needed. The problem is that, for these fibers, this region is too small, making it even difficult to distinguished, so it is not possible to calculate the Elastic modulus and hence, the bending stiffness.

5.3 Evaluation of results

Once the results of each experiment are shown, it is necessary to evaluate them and determine which fiber characterization is the most proper for the development of polymer stents.

5.3.1 Surface morphology

In the following table (Tab. 5.10), a comparison between the diameter and fineness of each fiber is shown.

Tab. 5.10: Surface morphology comparison

	Diameter ∅ [μm]	Fineness [dtex]
Yarn_Small	226	365.65 ± 4.79
Yarn_20	232	383.91 ± 12.92
Yarn_25	297.7	482.12 ± 25.47
Yarn_30	354.63	585.81 ± 30.22

As shown in Tab. 5.10, and as explained in Section 3, the higher the spinning pump speed, the larger the diameter and the fineness of each fiber. Moreover, the Yarn_Small diameter must be smaller than the others because the draw ratio of its process was so much higher than the other experiment ratio (9 > 1.36) and when the draw ratio increases, although the tenacity and fiber orientation improve, the cross-sectional area decrease.

5.3.2 Mechanical characterization

The comparison of the mechanical properties that have been extracted from the tensile test of each yarn is shown in the following table and in Fig. 5.6 and Fig. 5.7.

Tab. 5.11: Mechanical properties comparison

	Tensile strength [cN/tex]	Elongation at break [%]	Bending Stiffness ($x10^{-9}$) [$N \cdot m^2$]
Yarn_Small	65.24 ± 3.74	18.24 ± 1,43	420.67
Yarn_20	9.2 ± 0.68	645.89 ± 169,06	-
Yarn_25	9.02 ± 0.97	658.96 ± 153,7	-
Yarn_30	8.5 ± 1,06	688.38 ± 209,79	-

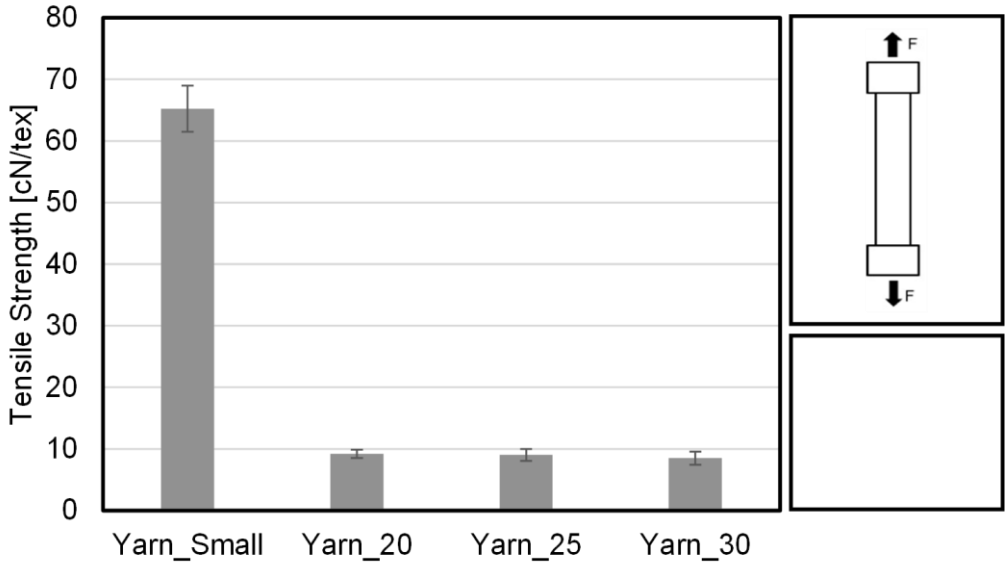


Fig. 5.6: Comparison of the Tensile strength of each yarn

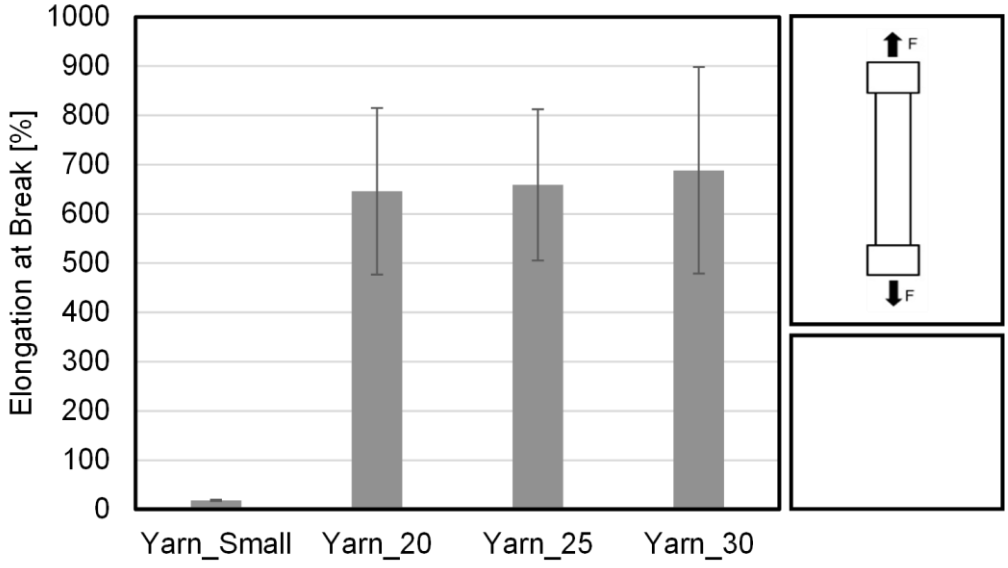


Fig. 5.7: Comparison of the Elongation at Break of each yarn

On the one hand, observing the average value of each parameter, it is observed how the tensile strength of the fibers produced on the small machine is higher than the ones produced in the large machine. The reason is that the achieved draw ratio was higher and therefore, the tenacity and fiber orientation too. However, the diameter of that fiber is not big enough (< 300 μm).

On the other hand, the fibers produced on the large machine have similar values of elongation at break and tensile strength, being these last values too low compared with the yarn of the small machine. It is normal, as because the draw ratio in this experiment is very low.

The diameter values that have been reached for the fibers of the large machine are, except for Yarn_20, close to or even above the required diameter. However, it is not a representative value, since if it had been possible to increase the draw ratio, the diameter would have been smaller.

6 Conclusion

In this work, a trial of developing a melt spinning process for polypropylene monofilaments has been performed. For the production of a fiber with a high bending stiffness for the manufacture of a stent, two experiments have been performed.

The first experiment was carried out in the melt spinning machine called “KSE”. This experiment aimed to obtain adequate parameters of the process to the adaption to the other experiment and machine. The results are good, above all regarding the mechanical properties of the fiber. The reason for these good results is the high value of the draw ratio that was achieved. Concerning the diameter, the achieved value was also acceptable, even though, it is below the requirement of 300 µm.

Besides, in spite of the fact that this machine is intended to be used for medical fibers, the addition of nanoparticles is not possible. The experiment is intended for the addition of nanoparticles of iron oxide in the future since it is the idea for the solution exposed in the introduction, so, it is necessary to transfer the experiment to the machine called "Bicomponent".

Regarding the second experiment in the Bicomponent machine, many results could not be obtained. Due to the failure in the winder system and the lack of availability of the Bicomponent machine, just one value of draw ratio could be tested, so the mechanical properties of those fibers are still insufficient. However, for this draw ratio, the values of diameter were acceptable, even above the requirement in the case of 30 rpm of spinning pump speed.

7 Outlook

With this work, a foundation is built for future research. Since the results of the first experiment were satisfactory, the next step is the adaptation of these results to the Bicomponent machine, trying to improve even more the fiber characterization, such as achieve a larger diameter for example.

If that step is reached successfully, a further step might be the addition of the nanoparticles to the production process of the fibers.

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9 Statement of academic honesty

Hiermit erkläre ich, dass ich die vorliegende Arbeit selbständig angefertigt habe. Es wurden nur die in der Arbeit ausdrücklich benannten Quellen und Hilfsmittel benutzt. Wörtlich oder sinngemäß übernommenes Gedankengut habe ich als solches kenntlich gemacht.

I hereby declare to the best of my knowledge that this thesis contains no material previously published or written by any other person. The work submitted in this thesis is the product of my own original research, except where I have duly acknowledged the work of others.

Aachen, 29/07/2019 _____

Ort, Datum — Unterschrift

City, Date — Signature

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