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Recycling plastic waste to purify water

Development of plastic waste derived membranes for sustainable, low-cost water filtration

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Preface

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Contents

Abstract

Water scarcity and plastic waste are two well-known, global problems. For **plastic waste**, an increase in recycling is necessary, which requires a perception change towards recycled plastics. For **water scarcity**, treatment and reuse of wastewater is the most promising option to decrease water consumption. Within this scope, membrane technology is an attractive method to accomplish this in a cost-efficient manner. However, today membrane technology is not applied to its full potential in industry.

This thesis research aims to develop a new generation of cheaper, green membranes, by **studying the use of a new source for membrane materials: plastic waste**. This research can lead to a cost-effective and more sustainable membrane technology. Both factors are essential in incentivizing industry to implement membrane technology.

A three-step approach is adopted to achieve this goal:

1. Fundamental study of plastic waste derived membranes. Based on experimental analysis with an aqueous dye solution, various membranes derived from post-consumer plastic waste are evaluated for retention and permeability. For two waste polymers - polystyrene (PS) and acrylonitrile butadiene styrene (ABS) - it is found that retention is close to or slightly below commercial nanofiltration (NF) membranes, while permeability is slightly better.

2. Investigation of the scalability. The scalability of the technology is investigated based on expert interviews and lab experiments. Seven negative effects of using plastic waste are identified and solutions are proposed. A prominent technical problem is the inconsistency of post-consumer waste, leading to a variable membrane quality. The proposed solution is the use of more consistent post-industrial waste.

3. Investigation of the applicability. The technical potential of membranes derived from post-industrial plastic waste for NF and ultrafiltration (UF) is evaluated based on indicative experiments with an aqueous dye solution and an aqueous beads solution. PS-waste derived membranes seem suitable for less demanding NF applications. ABS-waste derived membranes show much potential for high-quality UF.
The commercial potential of the membranes is evaluated, by developing a business model for the new technology from a university spin-off perspective. This business model is analyzed using an integrated economic model and is found to be feasible and attractive, mainly because of low resource costs and a well-chosen market position that allows efficient focusing of sales efforts.

Overall, this thesis shows that membranes derived from post-industrial PS and ABS waste have potential for industrial application and that a spin-off to commercialize them is feasible.

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List of Abbreviations

ABS	Acrylonitrile butadiene styrene
COGS	Cost of goods sold
DIPS	Diffusion-induced phase separation
DSC	Differential scanning calorimetry
EPS	Expanded polystyrene
GAE	General & administrative expenses
MF	Microfiltration
MWCO	Molecular weight cut-off
NF	Nanofiltration
NG	Nucleation and growth
NGO	Non-governmental organization
NMP	1-Methyl-2-pyrrolidone
OEM	Original equipment manufacturer
PA	Polyamide
PC	Polycarbonate
PE	Polyethylene
PES	Polyethersulfone
PESH	Hydrophilic polyethersulfone
PET	Polyethylene terephthalate
PP	Polypropylene
PPH	Product coverage - sales presence - hit rate
PS	Polystyrene
PVC	Polyvinyl chloride
PWP	Pure water permeability
RO	Reverse osmosis
SD	Spinodal decomposition
SEM	Scanning electron microscopy
SMEs	Small and medium-sized enterprises
TFC	Thin-film composite
TIPS	Thermally induced phase separation
UF	Ultrafiltration
USP	Unique selling proposition
VAT	Value-added tax
VIPS	Vapor-induced phase separation
W&WWT	Water & wastewater treatment

Chapter 1

Introduction

In this introduction, the problem is described, the research objective is stated, and the approach to achieve the objective is given.

1.1 Problem statement

This thesis research aims to address two global challenges: **water scarcity** and **plastic waste**.

1.1.1 Water scarcity

Global population has tripled during the 20$^{\text{th}}$ century. Experts argue about the capacity of the Earth to feed the increasing human populations. Can the Earth produce enough food for 10 billion people? 12 billion? In any case, it is found that the main factor limiting future food production is water. [7]

As populations increase, water consumption follows. Available water resources are increasingly diminished: groundwater is being depleted, pollution has outpaced the capacity of ecosystems to respond, and the effects of climate change are compounding the problem [7,8]. It is estimated that by 2025, assuming a ”business as usual” scenario, more than fifty countries (three billion inhabitants) will be confronted with water scarcity. It is clear that the world will soon face an unprecedented challenge of water scarcity. [9, 10]

In some regions, this challenge is already a reality. For example, in the northern part of China, overuse of water has caused thousands of rivers to dry up and has transformed grain-growing areas around Beijing to arid fields [11]. Similar water scarcity problems are occurring in California (US), Colombia, Pakistan, Somalia, Guatemala, Kenya and Australia [12]. In spite of this, most citizens in high-income countries undervalue water, leading to overconsumption. In Australia for example, over 50% of domestic water is used for gardening [9].

However, the increasing cost of water and stricter environmental regulations are major drivers to reduce water use. Industries that consume large quantities of water are encouraged to treat and reuse their own wastewater. This **internal water recycling** is the most promising option to decrease water consumption [13].

New technologies are needed to achieve internal water recycling in a cost-effective way.

1.1.2 Plastic waste

Since the 20th century, plastic has become the most common material in the world. Global plastics production grew from 1.5 million tons in 1950 to 265 million tons in 2010 [14, 15]. Unfortunately, favorable properties of plastic such as its durability and low cost, make plastic waste very problematic. The durability of plastic means that it persists in the environment for a very long time, and the low cost discourages recycling. [14, 16]

Plastic waste poses numerous problems and hazards. One major issue is large landfills in developing countries. These dumps pose serious threats to the environment and human health [14, 15]. Another major problem is ocean littering. Three million tons of floating plastic are trapped in the Pacific Ocean, covering an area double the size of France [17]. Sunlight and mechanical abrasion break the polymers down into small pieces or micro plastics. This creates a so-called ”plastic soup” of micro plastics. Upon ingestion, these micro plastics – and their chemical additives – are absorbed by organs, tissues and cells. This is not only harmful to the affected animal, but also indirectly harmful to other animals and humans through predator-prey interaction. [14, 18–21]

Various strategies are available to mitigate plastic waste: the best option is to prevent the creation of plastic waste. This option should be pursued, but is limited to certain applications. A good example is the restriction of single-use plastic bags in supermarkets in favor of reusable bags [18]. The second preferred option is **recycling of the plastic material**. This is more widely applicable, but not yet pursued to its full potential.

An increase in recycling is necessary, for both economic and ecological reasons. This requires a perception change towards recycled plastics.

1.2 Membrane technology

As mentioned, treatment and reuse of wastewater is the most promising option to decrease water consumption. Conventional methods, such as coagulation/flocculation, biological treatment, and sand filtration are widely used in industry, but this is currently changing because of two main incentives [6, 13]:

1. Shifting policy. Modern EU policy (Water Framework Directive, Drinking Water Directive, *etc.*) creates the need for more efficient and higher quality treatment processes. This has initiated a shift away from the use of chemicals due to their adverse environmental impacts. [6]

2. Need to reduce energy use and costs. Conventional methods require huge amounts of energy for heating and pumping processes. Due to increasing energy costs and EU commitments to the reduction of carbon emissions, new technologies are needed that reduce energy use. [6, 13]

Pressure-driven membrane processes provide an answer to both incentives, because of little need for chemicals and lower energy requirements. Additionally, membrane processes are cost-effective, selective, simple, compact and modular. They do not have transient periods (start-up, *etc.*), nor involve any phase change and are easy to scale-up (*e.g.*, by adding a parallel membrane). However, disadvantages for membranes are limited membrane lifetimes, the need for cleaning (because of fouling) and low fluxes. [7, 22, 23]

Remaining issue of membrane technology

When over fifty years ago the first synthetic membranes became available, the expectations for their technical and commercial relevance were very high. A multitude of potential applications were identified and a multi-billion dollar market was predicted for the membrane-based industry by the turn of this century [24].

The overall success of membrane technology, however, is lagging behind these expectations. In some applications, today's available membranes find it difficult to compete with conventional separation processes [25]. This means that for most businesses, the incentives for implementing new membrane technology remain rather low.

1.3 Research objective & methodology

Today, membrane technology has not reached its full potential, as the water & wastewater treatment industry is still hesitating to fully implement this new technology. For industry, two main incentives are essential to choose a new technology: costs and environmental sustainability [13, 25]. However, current membrane research is mainly focused on improving membrane performance and addressing technical membrane issues, and these two incentives (costs & environment) are generally not central objectives.

This thesis research, however, has a different research perspective. It aims to develop a new generation of cheaper, green membranes, by **studying the use of a new resource: plastic waste**. This fundamental change in research perspective can, in combination with existing research efforts, lead to cheaper and more environmentally sustainable membrane technology. These two factors are essential in incentivizing industry to implement membrane technology.

1.3.1 Research hypothesis & goal

The research hypothesis states the possibility to produce membranes from plastic waste. More specifically, it is hypothesized that membranes of industrial quality can be made for applications in ultrafiltration (UF) or nanofiltration (NF). This hypothesis is based on the preliminary results of an exploratory study, which shows that membranes produced from plastic waste can achieve high retention for small dye molecules in the size range of NF.

The aim of this thesis research is to validate this hypothesis by evaluating the potential of using plastic waste as a raw material for membrane technology in industrial applications. Ultimately, the goal is to bring this technology to application in industry, and this thesis should bring us closer to this goal.

1.3.2 Methodology

To achieve the goal of this research, three consecutive phases are established, each phase consisting of two specific objectives. This structure is visualized in figure 1.1, and provides a roadmap for the research.

FIGURE 1.1: Structure of the research

More specifically, the methodology consists of:

Phase I: study the fundamental potential of plastic waste derived membranes on lab-scale:

a. Validate the preliminary results of the exploratory study in a scientific manner.
b. Expand this experimental work to compare the results with commercial membranes.

Phase II: investigate the scaling up of the membranes from lab to industrial scale:

a. Identify the (negative) effects of using plastic waste as a resource on industrial scale.
b. Find and experimentally confirm solutions to the most critical issues found in (2a).

Phase III: evaluate the industrial applicability of the technology:

a. Experimentally investigate possible industrial applications of the membranes.
b. Evaluate the business potential of the technology and set the ground for a potential university spin-off.

This document is structured in the following way. Chapter 2 briefly introduces membrane technology and discusses membrane synthesis in more detail. Chapter 3 describes the materials and methods. Chapters 4, 5 and 6 present and discuss the results, according to the three-phase structure explained above. Finally, chapter 7 draws conclusions from the research and gives future prospects.

Chapter 2

Literature study

This chapter provides the necessary theoretical background of membrane technology for this thesis. It consists of 2 sections:

1. Broad introduction to membrane technology
2. In-depth analysis of membrane synthesis

2.1 Introduction to membrane technology

In essence, a membrane is a thin barrier that allows for the separation of certain compounds from a feed stream [1].

In this thesis research, the focus is placed on porous membranes. For these membranes, small pores within their structure perform a size exclusion: small molecules (*e.g.* water) pass through the pores, while larger compounds (*e.g.* bacteria) are blocked because of their size. This (simplified) mechanism is shown in figure 2.1.

Membrane processes are attractive techniques that allow separation of a wide range of components, ranging from suspended solids to small organic compounds and ions. Currently, the main application domain for membranes is water treatment, more specifically seawater desalination, wastewater treatment and drinking water production. [7,13,25]

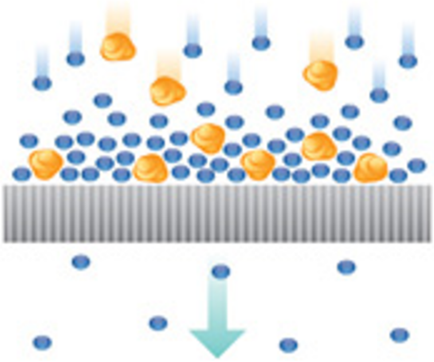

FIGURE 2.1: Size exclusion by a porous membrane [1]

2.1.1 General concepts

The mechanism presented above is simplified and does not cover all membrane processes. Generally, a membrane process can be defined as splitting a feed stream by a membrane into two fractions: the permeate, which is the fraction passing through the membrane, and the retentate, which is the fraction left behind. Membrane processes use a driving force (*e.g.* a pressure difference) to transport the permeate fraction through the membrane. [13]

In the case of pressure-driven membrane processes, the solvent (usually water) is transported through the membrane and dissolved compounds are (partially) retained based on their size, shape or charge. The separation efficiency is usually expressed by the **retention** of a given compound [13]:

$$R = \left(1 - \frac{C_p}{C_f}\right) \cdot 100\%$$

Where R is the retention (%), C_p the permeate concentration and C_f the feed concentration. The retention ranges from 0% for complete permeation to 100% for complete retention.

However, it is difficult to measure the retention for all possible components. Therefore, commercial membranes are typically provided with one summarizing performance indicator, the molecular weight cut-off (MWCO). The MWCO refers to the molecular weight of the molecule that is retained by the membrane with 90% efficiency [5].

The other important performance indicator of a membrane is the throughput or flux. This is typically expressed by the pure water permeability (PWP), which is a measure for the pure water flux through the membrane per unit of pressure difference [5]:

$$PWP = \frac{V_p}{A_M \cdot t \cdot P}$$

Where V_p is the permeate volume (l), A_M the membrane surface area (m^2), t the permeation time (h), and P the pressure (bar).

2.1.2 Classification

Membrane processes can be classified according to the driving force used in the process. The most relevant driving forces are (i) pressure difference, (ii) concentration difference and (iii) electric potential difference [25]. In this research, the focus is placed on pressure-driven membrane processes. These processes can again be classified based on the characteristics of the membrane (pore size) and the size of the retained molecules. This classification distinguishes microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) [10, 13]:

1. Microfiltration. MF membranes have the largest pores (0.1 µm - 10 µm), and retain micron-sized compounds like particles, suspended solids and yeasts. They also have the largest permeability, so that a sufficient water flux is obtained at low pressures (0.5 bar - 3 bar).

2. Ultrafiltration. UF membranes have smaller pores (2 nm - 100 nm) and can retain solutes with a diameter larger than a few nanometer, including large organic compounds, natural organic matter, colloids, and bacteria. Their permeability is lower, requiring higher pressures (2 bar - 10 bar).

3. Nanofiltration. NF membranes, which can be porous (typical pore size of 1 nm) or dense and may have a surface charge, are able to retain even smaller compounds, for example organic micropollutants. They require high pressures (8 bar - 30 bar) as driving force.

4. Reverse osmosis. RO membranes are dense membranes and can separate for example salts. The pressure needed as driving force is very high (10 - 80 bar) as the barrier becomes more dense.

Figure 2.2 shows a schematic representation of each process. For this thesis research, the scope is limited to MF, UF, and porous NF membranes. This is due to the fact that dense NF membranes and RO membranes are more technologically advanced, and therefore more difficult to produce than porous membranes.

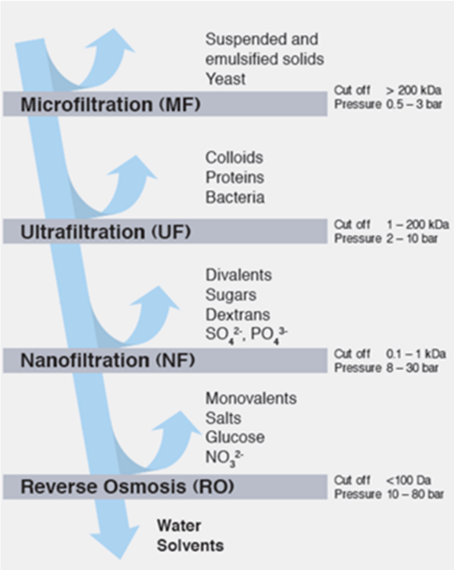

FIGURE 2.2: Schematic representation of MF, UF, NF and RO [2]

2.1.3 Applications of membrane technology

Pressure-driven membrane processes offer a wide spectrum of applications. Two major applications are drinking water production and wastewater treatment.

Conventional **drinking water production** includes coagulation, flocculation, sedimentation and sand filtration. These treatment steps can be replaced by a single UF step, or a combination of UF/MF with coagulation or activated carbon treatment. The pore size of UF membranes is sufficient to ensure efficient removal of suspended particles and colloids, turbidity, algae, bacteria, parasites, and viruses [13, 23]. Compared with the conventional technologies, membrane processes offer several advantages: little need of chemical agents, little sludge production, compact process, and easy automation. [26]

In **wastewater treatment**, any of the conventional methods described for drinking water production can again be replaced by UF or UF/MF. Additionally, NF can be applied specifically to remove color, organic micropollutants, degradation products from the effluent of biologically-treated wastewater, heavy metals, and nutrients, before discharge or reuse of the water. This is typically applied in water-intensive industries like the textile and dye, and the pulp and paper industries. [13]

Other applications are pre-treatment for reverse osmosis, clarification of fruit juice, pre-concentration of milk, chemical-free beer production (*e.g.* removal of yeasts and proteins), and pharmaceutical purification (*e.g.* proteins, vaccines, nucleic acids). [22, 27]

2.2 Membrane synthesis processes

The key requirements for membranes are high permeability and high selectivity. However, this should be accompanied by sufficient mechanical and chemical stability, low fouling tendency and cost-effective and defect-free production [13]. The membrane characteristics depend greatly on the properties of the materials and the process conditions [28].

A variety of production techniques and resource materials are available to meet these requirements. The production techniques can be broadly classified into two groups: (i) solvent-based methods and (ii) solvent-free methods.

In this thesis research, the main focus is placed on solvent-based methods, which are described in detail in this section. A short overview of alternative solvent-free methods is also given. First, the typical materials used for membrane production are discussed.

2.2.1 Membrane materials

The most commonly used membrane materials are polymers. However, membranes can also be made from ceramic materials. Also organomineral and metallic membranes exist, though they are less common. Polymers, such as polyacrylonitrile (PAN), polyvinylidene fluoride (PVDF), polyethersulfone (PES), polystyrene (PS), and polypropylene (PP), are commonly used. The main advantage is that polymers are cheap, which explains why they are almost always used in wastewater treatment. However, they require mechanical support and can have chemical stability problems when processing certain solvents. Most polymers are intrinsically hydrophobic, which decreases the water flux. [13, 22]

Ceramics, such as titanium dioxide (TiO_2), zirconium dioxide (ZrO_2), and alumina (Al_2O_3), do not have these disadvantages: they have good thermal and chemical stability, are stronger and more hydrophilic. However, they are more expensive (both in resource cost and in production cost), and are therefore not commonly used in wastewater treatment. Two special membrane types are organomineral and metallic membranes. The former type consists of an organic matrix with a ceramic filler. The latter is produced by sintering of stainless steel filaments, creating a very porous and robust membrane [22, 29]. In this thesis research, the scope is limited to **polymeric membranes**, since the goal is to obtain low-cost membranes.

2.2.2 Solvent-based membrane synthesis: phase inversion

Solvent-based membrane synthesis techniques are based on the principle of phase inversion. These techniques are often referred to as phase inversion, phase separation or polymer precipitation. Most commercially available membranes are prepared by phase inversion, because of its versatility and defect-free membrane production. [3]

The technique of phase inversion has been known for quite some time; the first paper on the preparation of porous membranes by phase inversion appeared in 1907 [3]. Phase inversion is executed by controlled phase separation of a homogeneous polymer solution into two phases: one with a high polymer concentration, and one with a low polymer concentration. The polymer-rich phase solidifies shortly after (or almost simultaneous with) phase separation, and forms the membrane solid matrix. The polymer-lean phase eventually forms the membrane pores. This phase separation of polymer solutions can be induced in several ways [3, 28, 30]. The four main techniques are:

1. Diffusion-induced phase separation (DIPS), often referred to as immersion precipitation. Phase separation is induced by immersing the polymer solution in a non-solvent bath where solvent is exchanged for non-solvent.
2. Thermally induced phase separation (TIPS). Phase separation is generated by cooling down the polymeric solution.
3. Vapor-induced phase separation (VIPS), is similar to DIPS, but non-solvent is absorbed from the vapor phase instead of from a liquid.
4. Air-casting of a polymer solution. In this process, the polymer is dissolved in a mixture of a volatile solvent and a less volatile non-solvent. The volatile solvent evaporates from the three-component mixture, causing precipitation as the system becomes enriched in polymer and its solubility is decreased.

The four techniques differ in the desolvation mechanism. In this research, membranes are synthesized using the DIPS technique, since this is the most common technique, easy to execute and available in the laboratory. The following sections discuss the DIPS method in more detail and explain the asymmetric membrane structure that follows from the DIPS method.

Diffusion-induced phase separation (DIPS)

In the DIPS process a thin layer of polymer dissolved in a solvent, is cast on a suitable support (*e.g.* a glass plate). Phase inversion is induced by immersing the polymer solution film in a non-solvent bath. Solvent and non-solvent are exchanged by diffusion: the solvent, having affinity for the non-solvent, diffuses into the non-solvent bath; the non-solvent diffuses in turn into the polymer solution. Figure 2.3 illustrates the film-bath interface during immersion. [3, 5, 31]

Subsequently, the composition of the polymer solution changes, becomes thermodynamically unstable and demixing takes place. The polymer solution is separated into two phases: a polymer-rich and a polymer-lean phase. Eventually, the polymer-rich phase is solidified into a solid matrix which forms the membrane structure, while the polymer-lean phase develops into the membrane pores. [3, 5, 31]

The concept of thermodynamic instability requires some more explanation. For simplicity, this explanation is limited to three components: non-solvent, solvent and polymer. However,

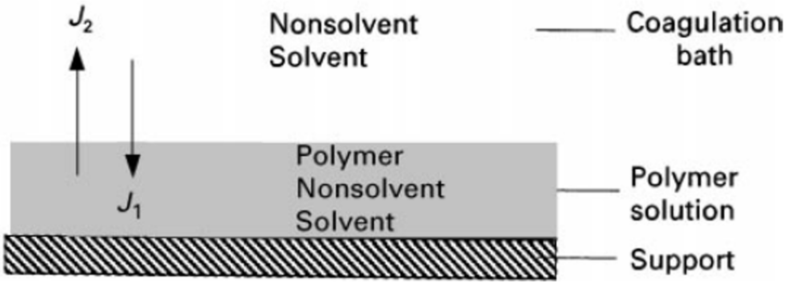

FIGURE 2.3: Schematic representation of the film-bath interface during phase inversion, with J_1 the non-solvent flux and J_2 the solvent flux [3]

in reality additives are often used in the process. Describing this would require quaternary systems and complex thermodynamic and kinetic descriptions. [3]

The phase inversion process of membrane formation is determined by the particular thermodynamic situation, but also by kinetic processes. This can be displayed using the Gibbs phase triangle. An example is given in figure 2.4. The Gibbs phase triangle in this figure contains a miscibility gap boundary (binodal) as well as a boundary between the metastable and unstable areas (spinodal). It also shows the possible pathways (A, B and C) of the mixture during phase inversion. Where and how it moves into the miscibility gap and the pathway within, determines the process of pore formation. [4]

The starting point is a homogeneous solution of polymer and solvent. When this solution is immersed in a non-solvent bath, the composition changes as non-solvent diffuses into the solution and solvent diffuses out. In the phase triangle, this can be seen as moving in the direction of pure non-solvent. However, the slope of this pathway can be different (path A, B and C). The kinetics of the diffusion process, and more specifically the ratio in-diffusion of non-solvent and out-diffusion of solvent determines this slope. The speeds of diffusion are determined by the affinity of the solvent for the non-solvent, and the concentrations in the polymer solution and the coagulation bath. [4, 32, 33]

The mechanism of phase separation within the metastable area between binodal and spinodal (path A and C) is different from that inside the unstable area (path B). The former mechanism is called nucleation and growth (NG), the latter is called spinodal decomposition (SD) [4]. During NG, nuclei of the minor phase are formed in a matrix of the major phase. In the case of path A the nuclei consist of the polymer-lean phase. These droplets can grow further until the surrounding continuous phase solidifies via crystallization, gelation or vitrification. Coalescence of the droplets before solidification leads to the formation of a porous structure. Path C cannot lead to membrane formation, because in this case the nuclei consist of the polymer-rich phase. During SD (path B), the first stages of phase inversion consist of a co-continuous structure of the segregated phases from which the final pores are formed on further penetration into the miscibility gap. [3, 4, 32, 33]

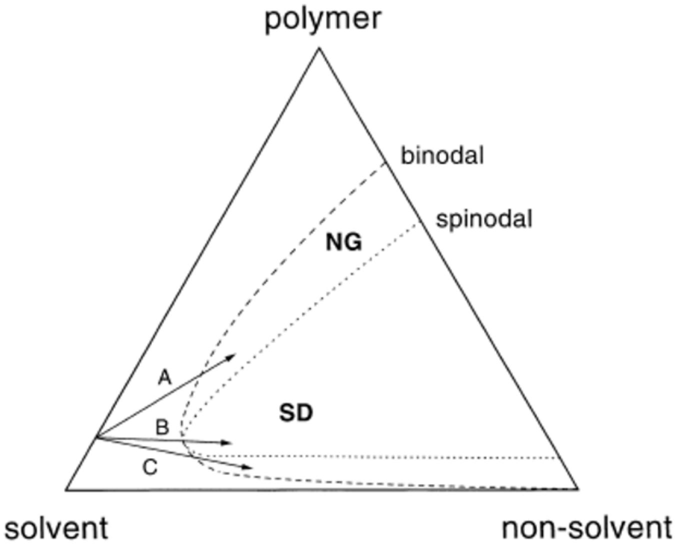

Figure 2.4: Different pathways of a binary casting solution into the miscibility gap of a ternary membrane forming system [4]

It is clear that both kinetics and thermodynamics play an important role during the process of membrane formation. Changing the preparation factors during the process may have an influence on kinetics, thermodynamics, or both, resulting in a different membrane structure and a different membrane performance. The factors that have an influence are extensively studied and reviewed in literature and are listed here [5, 22, 34]:

1. Choice of polymer: the polymer type influences thermodynamics and kinetics; it has an effect on the shape of the Gibbs phase triangle and influences the rates of diffusion of solvent and non-solvent.
2. Polymer concentration: increasing the polymer content leads to a lower porosity of the membrane and therefore to a lower permeability.
3. Additives: pore-forming agents, such as polyvinylpyrrolidone, can be added to the polymer solution to increase the water flux. Volatile components, such as acetone, lead to a denser top layer. Additives can also be added to the non-solvent bath (*e.g.* alcohols) to alter the thermodynamics and kinetics.
4. Choice of solvent: the solvent type influences thermodynamics (Gibbs phase triangle) and diffusion kinetics (affinity for the non-solvent).
5. Choice of non-solvent: the non-solvent type also influences thermodynamics and diffusion kinetics.
6. Temperature of the non-solvent bath: thermodynamics and kinetics are typically temperature dependent.
7. Relative air humidity: water vapor in the air can cause phase separation, prior to immersion in the non-solvent bath.

By varying all these preparation parameters, an optimized membrane for a specific purpose can be obtained.

Asymmetric membrane structure

The reason why phase inversion is so commonly used is that membranes prepared by phase inversion have an asymmetric pore structure, which was first observed by Loeb and Sourirajan in 1963. These membranes consist of a very thin, microporous surface layer (0.1 µm - 1 µm) which is supported by one or more thicker layers with larger pores. The supporting layers do not contribute to the resistance against mass transfer, but provide mechanical strength. The thin surface layer determines permeability and selectivity and, because it is so thin, the membrane demonstrates significantly improved fluxes. This asymmetric membrane structure allows for a combination of high flux and sufficient mechanical strength, and was essential for the industrial breakthrough of membrane filtration. [13, 35, 36]

The formation of an asymmetric structure can be understood based on the concept of supersaturation. The top layer of the polymer solution rapidly absorbs non-solvent, and becomes quickly supersaturated with respect to the polymer. This leads to a rapid precipitation from many nucleation sites and a short time between precipitation and solidification, forming a finely porous structure. [37]

The precipitated polymer in the top layer slows down further exchange of solvent and non-solvent, causing slower entry of non-solvent in the sublayer. Therefore, the degree of supersaturation in the sublayer is lower. This leads to a slower precipitation from fewer nuclei, and a longer time between precipitation and solidification, leading to a coarser structure. Thus, further into the membrane structure, progressively larger agglomerates are formed, leading to larger pores and an asymmetric structure. [37]

2.2.3 Solvent-free membrane synthesis

The phase inversion process requires a solvent, which is usually an expensive and hazardous chemical (*e.g.* NMP). The need to reduce costs and improve safety, stimulates the search for alternative solvent-free processes. However, only a few solvent-free membrane synthesis techniques are known. [38]

The melt extraction and cold-stretching method is a low-cost method based on the extrusion of semi-crystalline polymer films or hollow fibres followed by stretching. A problem with this method is that it can only be used for specific polymers and that it is difficult to control. [22, 35, 38]

Radiation track etching consists of shooting (radiation) on the polymer. The track etching enables the production of membranes with parallel pores in cylindrical form which have an identical diameter. However, it has limited applications in the manufacture of flat membranes due to its poor permeability and high cost. [22, 35, 38]

Sintering polymer powders in the form of membranes is an alternative method. In essence, the different polymer grains are melted together by applying heat to form the membrane matrix and the interstitial space between the grains forms the membrane pores. The grain size is essential for uniformity and quality, which is one of the reasons why it is difficult to obtain reproducible membranes, though promising results have been found using this technique. [22, 39]

Chapter 3

Materials and methods

3.1 Materials

In this work, both post-consumer and post-industrial plastic waste materials are studied. Five post-consumer plastic waste materials are obtained from personal use, and fourteen post-industrial plastic waste materials are obtained from Indaver, a Belgian waste collection company. The post-consumer plastic waste materials are selected based on (i) the availability in post-consumer waste and (ii) the exclusion of some polymers based on the results of an exploratory study (see section 4.1). The selection comprises three CD-cases (PS and PVC based), single-use plates (EPS based) and LEGO® toy bricks (ABS based). For the post-industrial plastic waste materials, a broad selection is made of the available post-industrial waste streams at Indaver. This selection includes six polymers (PS, ABS, PA, PP, PE and PET) in various product shapes (trays, pellets, foils, *etc.*)

The selected materials and their identification labels are listed in table 3.1. To stress the origin of the materials, the identifications can be preceded by a prefix: ”SELF-” for post-consumer plastics (obtained from personal use); ”IND-” for post-industrial plastics (collected by Indaver).

Besides plastic waste, two other raw materials are needed in order to produce membranes. 1-Methyl-2-pyrrolidone (NMP, 99%), the polymer solvent, is purchased from Sigma Aldrich and used without further purification. A non-woven carrier material (Novatexx 2471 PP/PE) is obtained from Freudenberg.

3.2 Membrane synthesis

To prepare membranes, the immersion-precipitation procedure described by Boussu et al. [5] is followed. The waste materials are first cleaned, dried and cut to pieces (of about 1 cm). The waste materials are dissolved in the solvent, NMP, by heavy stirring for several days to obtain a homogeneous solution. A thin film of the polymer solution is made on a support using a filmograph (K4340 Automatic Film Applicator, Elcometer) at a speed of approximately 10 mm/s. This is performed in an atmosphere with a controlled relative humidity of 20% - 30% to enhance reproducibility [5]. The polymer solution film has a thickness of 250 µm to obtain defect-free membranes [5]. The support is a glass plate with the non-woven support layer (Novatexx 2471 PP/PE) taped onto it. Before casting, the

Table 3.1: Identification labels and polymer types of plastic waste materials

post-consumer plastic waste		post-industrial plastic waste	
label (SELF-)	polymer type	label (IND-)	polymer type
CD-1	PS	PS-A	PS
CD-2	PVC	PS-B	PS
CD-3	PS	PS-C	PS
Plates	EPS	PS-D	PS
LEGO®	ABS	PS-FR	PS[1]
		ABS-A	ABS
		ABS-B	ABS
		PA	PA
		PP-A	PP
		PP-B	PP
		PP-C	PP
		PE-A	PE
		PE-B	PE
		PET	PET

non-woven support is wetted with the solvent to prevent polymer intruding its pores [5].

The casted film is, immediately after casting, immersed in a non-solvent bath of distilled water at room temperature. Here, the phase separation starts and a porous membrane is formed. After 60 minutes of immersion, the membrane is washed with distilled water. Circular shapes are cut from the membrane and stored in ultrapure water (type 1 ”milli-Q water”, Millipore Corporation). A more detailed discussion of the immersion-precipitation (phase inversion) process can be found in section 2.2.2.

3.3 Membrane evaluation

The membranes are evaluated at three levels: operational, economic, and membrane performance. On the operational level, plastic waste materials are evaluated on their processability and dissolvability. On economic level, material cost and transport costs are the most important parameters.

The membrane performance is tested in a dead-end set-up (Sterlitech HP 4750 stirred cell). In this module, the feed solution is contacted with the membrane surface (effective membrane area of 14.5 cm^2). A pressure of 6 bar is exerted on the feed solution by an inert nitrogen gas. An IKAMAG REO magnetic mixer from Drehzahl Electronic is used at 700 min^{-1} to provide turbulence in the feed solution close to the membrane surface. The set-up is shown in figure 3.1.

Two membrane performance indicators, pure water permeability and retention, are determined. In a first step, the module is filled with distilled water and the pure water permeability is calculated using the following equation:

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[1] The PS-FR material consists of PS with most likely an added fire retarding (FR) component

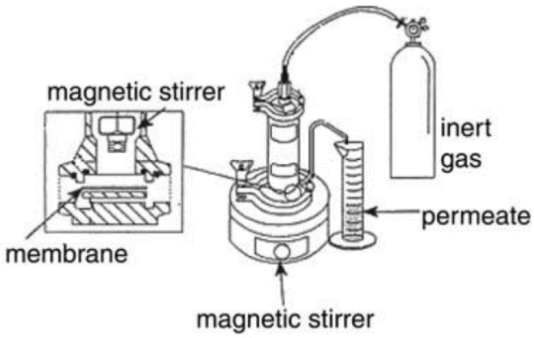

Figure 3.1: Schematic representation of the dead-end set-up [5]

$$PWP = \frac{V_p}{A_M \cdot t \cdot P}$$

Where V_p is the permeate volume (L), A_M the membrane surface area (m^2), t the permeation time (h), and P the pressure (bar). The PWP is only recorded after approximately one hour of permeation, to eliminate transient effects like membrane compaction. [40]

Alternatively, the permeability can be determined for a specific solution (*e.g.*, an aqueous dye solution) instead of distilled water.

Secondly, the retention is determined for two specific solutes. Based on exploratory research, it is expected that the membranes are in the UF-NF range. Therefore, solutes are chosen that correspond to NF: dyes. Aqueous dye solutions are interesting to use as feed solution: they have a challenging molecular size for NF, the dye color provides a quick visual indication of the membrane performance, quantitative analysis with UV-spectrophotometry is possible, and dye filtration also represents an important industrial application for NF.

The module, containing the same membrane (which is already compacted), is filled with an aqueous dye solution. The dyes 'malachite green oxalate' (obtained from VWR) and 'congo red' (obtained from Avocado Research Chemicals Ltd.) are studied. More information on the aqueous dye solutions is provided in table 3.2. Malachite green oxalate is chosen because of its large molecular weight, and congo red because it can be compared with experimental results from Boussu et al. (see section 3.3). The retention of these components can be calculated using the following equation:

$$R = \left(1 - \frac{C_p}{C_f}\right) \cdot 100\%$$

Where R is the retention (%), C_p the permeate concentration and C_f the feed concentration.

The concentrations of the component in the feed and permeate are determined with UV-visible spectrophotometry (UV-1601, Shimadzu). A standard curve is determined for both components, and proved to be linear in the used concentration range, following the law of Lambert-Beer. Standard curves are provided in appendix A.

Table 3.2: Characteristics of the aqueous dye solutions

Dye name	Molar mass	Concentration
Malachite green oxalate [41]	827 g/mol	14 ppm
Congo red [42]	697 g/mol	14 ppm

Reference: commercial NF membranes

To have a reference, characterization data of commercial NF membranes are necessary. These data have been obtained by Boussu et al. [5] by testing a selection of commercial NF membranes. It concerns the membranes N30F and NFPES10 from Nadir, Germany. According to the manufacturer, the MWCO of N30F and NFPES10 is, respectively, 400 Da and 1000 Da [5]. Four lab-prepared, virgin polyethersulfone (PES) based NF membranes are added to this selection. Boussu et al. have characterized this selection of membranes by determining the retention of the dye congo red and the pure water permeability. These characteristics are used as a reference for NF throughout this thesis research.

Membrane evaluation: MF & UF

A selection of plastic waste derived membranes are evaluated for microfiltration and ultrafiltration. This is done by measuring the retention for two solutions of beads. For evaluating microfiltration, an aqueous solution of fluorescent beads of 1 µm mean particle size (obtained from Sigma Aldrich) was used. For evaluating ultrafiltration, an aqueous solution of fluorescent beads of 30 nm mean particle size (obtained from Sigma Aldrich) was used. More information about the aqueous beads solutions is provided in table 3.3.

Table 3.3: Characteristics of the aqueous beads solutions

Beads type	Mean particle size	Concentration
Latex beads, amine-modified polystyrene	1 µm	100 ppm
Latex beads, carboxylate-modified polystyrene	30 nm	500 ppm

The concentration of fluorescent beads in feed and permeate can be detected using UV-spectrophotometry. A standard curve is determined and proved to be linear in the used concentration range, following the law of Lambert-Beer. Standard curves are provided in appendix A.

Every membrane performance experiment is performed three times, unless otherwise mentioned.

Other analysis methods

SEM The membrane morphologies are inspected by SEM (scanning electron microscopy, XL30 FEG SEM, Philips, Eindhoven, Netherlands). The membrane preparation for SEM involves the following steps: after drying, the membrane samples are dipped in liquid nitrogen and cracked. This allows to obtain an untouched cross section for SEM analysis. The membranes are sputtered with a thin conductive layer of palladium/platinum. This is followed by degassing in a vacuum oven.

DSC The thermal behavior of the plastic waste streams is determined by DSC (differential scanning calorimetry, DSC Q 2000, TA Instruments) to obtain an indication of the chemical composition. Samples with masses of approximately 7 mg are placed in aluminum pans and measured at a heating and subsequent cooling rate of 10 °C/min.

Rheometry The viscosity of the plastic waste streams is determined by rheometry (AR 2000ex rheometer equiped with electrically heated plates, TA Instruments). The plastic waste stream samples are first compression molded to 25 mm discs, dried in vacuum overnight and measured in an inert nitrogen atmosphere.

Chapter 4

Phase I: Fundamental study

"Can membranes be made from plastic waste?"

This chapter tries to provide an answer to this fundamental question and forms the experimental basis for the rest of the thesis research. The question was first asked in 2011 by Prof. Bart Van der Bruggen to a group of bachelor engineering students (myself among them) in the context of a university group project. Looking back now, this group project was a first exploratory study. In this thesis research, the experimental work initiated by the exploratory study is validated to acquire quantified, scientific results and expanded to be able to compare with commercial membranes.

In this first phase, the focus is on fundamental lab-scale research: trying to develop membranes using post-consumer plastic waste. In later phases, the focus moves towards scale-up and application of the technology.

The first section of this chapter discusses the exploratory study, as executed by the university project group. The second section discusses the validation of the experimental results. The third section discusses the expansion of the experimental study to compare with commercial membranes. The fourth section establishes a production procedure that allows for the production of reproducible, defect-free membranes.

4.1 Exploratory study

The exploratory study comprises of a 3-month university group project, of two groups of 2nd bachelor engineering students at KU Leuven, executed in the fall of 2011. The goal of the group project was to use plastic waste to develop membranes for water filtration.

4.1.1 Research content

The exploratory research consists of collecting various post-consumer plastic waste materials, producing membranes using the immersion-precipitation procedure, varying different production parameters and testing the performance of the membranes.

The following post-consumer plastic waste materials are selected:

1. CD-cases (PS)
2. Yoghurt containers (PS)
3. Cushioning material for packaging (brand name Isomo®) (EPS)

4. LEGO® toy bricks (ABS)
5. CDs (PC)
6. Lab gloves (PVC)
7. Piping material (PVC)

The membrane performance is evaluated by determining retention and permeability of an aqueous dye solution (malachite green oxalate, 0.3 ppm). A number of membrane production parameters are varied and their influence on membrane performance is evaluated:

1. Composition of the polymer solution: the range 15 wt% - 35 wt% polymer in solvent is tested.
2. Membrane casting thickness: 100 µm, 150 µm, 200 µm, and 250 µm are evaluated.
3. Support layer: a Novatexx 2471 PP/PE support layer and no support layer are tested.
4. Coagulation medium: distilled water, a salt solution, and phase inversion in ambient air are evaluated.

4.1.2 Results

Unfortunately, during this thesis research it is found that the methods to test retention and permeability used during the exploratory research are not scientifically correct (see section 4.2). As a consequence, the results obtained by the exploratory study cannot be used as such. Validation of the experiments is needed and is discussed in section 4.2.

However, the results obtained by the exploratory research should not be thrown away – once validated, they can still be useful (*e.g.* in showing qualitative differences).

The exploratory study results in three successful raw materials and an analysis of the four production parameters. CD-cases (PS), Isomo® (EPS) and LEGO® (ABS) seem to be good raw materials for producing membranes. The other materials are not (sufficiently) soluble in NMP to synthesize membranes. A 25 wt% polymer solution produces the best tentative results, in an investigated range of 15 wt% - 35 wt%. Using a support layer (Novatexx 2471 PP/PE) significantly reduces the brittleness of the membrane, which is an issue when no support layer is used. Therefore, a support layer is preferred. Distilled water as coagulation medium produced the best tentative results. The tentative experimental results are shown in table 4.1, though it is again stressed that the results should not be used as such.

Table 4.1: Tentative experimental performance of post-consumer plastic waste membranes for malachite green oxalate found in the exploratory study

raw material	retention [%]	solution permeability $[L/m^2/h/bar]$
PS (CD-cases)	96.5% – 99.3%	6.8 – 18
EPS (Isomo®)	91.6% – 97.2%	15 – 96
ABS (LEGO®)	75.6% – 93.5%	26 – 427

4.2 Experimental validation

Due to incorrect use of testing methods, the results obtained in the exploratory study are not directly useful and need to be validated. In this section, first the problems concerning the university group project are identified and explained. Then, the correct test results obtained during this thesis research are shown and discussed.

4.2.1 Problems concerning the exploratory study

The exploratory study, consisting of a university group project of 2nd bachelor engineering students, lacked a thorough literature study of the scientific methods to evaluate membrane performance. In this thesis research however, a literature study has been performed and a correct testing methodology is found. It is described in section 3.3.

Two incorrect methods are used in the exploratory study. Firstly, the determination of the permeability happened immediately, by measuring the flux through the membrane during the first 10 mL of permeation. However, in the beginning of permeation the membrane is being compacted by the exerting pressure. This causes the membrane to become denser, reducing the flux until the membrane reaches its final, reduced thickness. To take this effect into account, in this thesis research all membranes are subjected to 60 minutes of compaction by a pressure of six bar before recording the permeability. Not taking this effect into account leads to overestimation of the permeability.

The second incorrect method is the determination of the retention: only the first 10 mL of permeate is collected and tested. However, during the initial permeation, the dye adsorbs to the surface of the membrane. Only after approximately 10 mL, the surface is saturated and the actual permeation begins. Therefore, this paper argues that only collecting the first 10 mL of permeate can lead to an overestimation of the retention of the membrane.

This hypothesis is supported by the following experimental observation: when the membrane is taken out of the module after 10 mL of permeation of the dye solution, the color of the membrane visibly changed, which is caused by adsorption of the dye onto the polymer. Figure 4.1 shows the membrane surface before and after permeation. This phenomenon demonstrates that collecting the permeate too early leads to an overestimation of the retention.

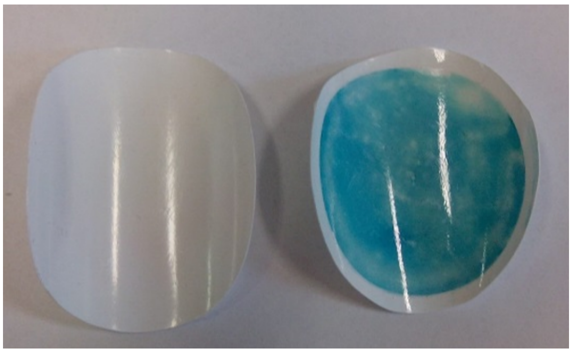

Figure 4.1: Adsorption of dye on used membrane (right) compared to fresh membrane (left)

To avoid interference of this transient adsorptive effect, in this thesis research first 50 mL is permeated and only afterwards the permeate is collected for concentration determination.

4.2.2 Validation

To validate the exploratory study, new experiments are conducted using the scientifically correct methods described in section 3.3. However, some of the information of the exploratory study can still be used as first indication of where to look and to narrow down the number of varying production parameters.

Production parameters

The number of post-consumer plastic waste materials can be narrowed down to the following three. The other materials proved to be insoluble in the solvent, NMP.

1. CD-cases (PS)
2. Single-use plates (EPS) (instead of Isomo®, but similar material)
3. LEGO® (ABS)

Four production parameters are tested in the exploratory study. Based on the tentative experimental results, one choice for each parameter is made:

1. Composition of the polymer solution: **25 wt% polymer** - 75 wt% solvent (NMP). This composition can be varied in a next stage, when trying to optimize the membranes.
2. Membrane casting thickness: the exploratory study suggests 100 µm. However, this is changed to **250 µm** because a larger thickness is less prone to defects [5].
3. Support layer: a Novatexx 2471 PP/PE **support layer** is preferred above no support layer to obtain defect-free membranes.
4. Coagulation medium: **distilled water** gave the best results. This can be further investigated in a next stage, when trying to optimize the membranes.

Validation results

In this validation, the membranes are synthesized (using the production parameters given above) and are experimentally evaluated for the following two factors:

1. Retention of an aqueous dye solution (malachite green oxalate, 14 ppm)
2. Permeability for the aqueous dye solution

The results of these experiments are shown in table 4.2. The retention of the membranes is found to be in the range 70% - 90%. The PS (CD-cases) membranes are in the lowest part of this range, the EPS (plates) membranes in the middle, and the ABS (LEGO®) membranes in the highest part. Compared to the exploratory study, the retention values of table 4.2 are much lower and also the trend (ABS<EPS<PS) is reversed. These results show that the exploratory study significantly overestimates the retention of the membranes. The fact that the trend is reversed may be due to using a different waste product as raw material for the PS, EPS and ABS membranes in this validation compared to the

exploratory study (*e.g.* a different type of CD-case).

The dye solution permeabilities range from 7 - 18 L/m^2/h/bar. The dye solution permeabilities for the PS (CD-cases) membranes are similar to those found in the exploratory study. For the EPS (plates) and ABS (LEGO®) membranes however, the dye solution permeability is much lower than the values found in the exploratory study, indicating an overestimation in the exploratory study. Moreover, the values found in the exploratory study have a very broad range and are extremely high, suggesting these values are not correctly measured. Also, the trend of the permeabilities (PS>EPS>ABS) is reversed in the exploratory study. This may again be due to using different waste materials.

Although the experimental results of table 4.2 look reasonably good, it is difficult to tell whether these membranes are really promising. Therefore, the experimental research must be continued and expanded, to obtain information on the membrane performance that can be compared to the performance of commercial membranes. This is discussed in the next section.

TABLE 4.2: Experimental performance of post-consumer plastic waste membranes for malachite green oxalate

raw material	retention [%]	solution permeability $[L/m^2/h/bar]$
PS (CD-3)	71% – 81%	12 – 18
EPS (plates)	76% – 87%	8.8 – 11
ABS (LEGO®)	84% – 90%	6.9 – 8.4

4.3 Experimental verification

To experimentally verify the potential of the plastic waste derived membranes, it is necessary to compare their performance with commercial membranes. Most manufacturers only give limited information (*e.g.* only the molecular weight cut-off (MWCO) value, which is difficult to obtain experimentally). Fortunately, Boussu et al. [5] have characterized a selection of commercial NF membranes by determining the pure water permeability (PWP) and retention for an aqueous dye solution (congo red, 14 ppm). More detailed information about the selection of commercial membranes is provided in section 3.3.

Therefore, in this experimental verification, membranes are tested for retention of the same aqueous dye solution and for pure water permeability. The same production parameters as for the validation are used. The results of these experiments, together with the reference values for commercial NF membranes, are listed in table 4.3.

Based on retention, the PS (CD-cases) membranes belong to the top part of the range for commercial NF. Also for the PWP, they belong to the upper part of the commercial NF range. The EPS and ABS membranes are similar and have a retention slightly below the commercial NF range. Their PWP is rather in the middle of the commercial NF range.

Overall, these experimental results show that membranes derived from plastic waste are relatively close to commercial NF membranes for the filtration of the specific aqueous dye solution. This is of course only one application - a complete analysis would require multiple types of dyes and other solutes. However, the results show that these membranes, and especially the PS membranes, are fundamentally promising for commercial NF.

Table 4.3: Experimental performance of post-consumer plastic waste membranes for congo red compared to a selection of commercial NF membranes

raw material	retention [%]	pure water permeability $[L/m^2/h/bar]$
PS (CD-3)	97% – 98%	15 – 33
EPS (plates)	87% – 93%	12 – 16
ABS (LEGO®)	83% – 98%	11 – 28
Commercial NF	92% – 99%	3.0 – 25

4.4 Defect-free membrane production

An important aspect of membrane development is to establish a production procedure that allows for the production of reproducible, defect-free membranes. The immersion-precipitation method, as described in literature [5], does not necessarily achieve this. This is because some production parameters are not mentioned or not explicitly specified.

A troubleshooting approach is adopted: based on a systematic search for the source of various issues encountered during experimental membrane synthesis, six practical measures - in addition to the existing immersion-precipitation method - are found to be essential in manufacturing consistent, good quality membranes. They are listed in appendix B.

4.5 Conclusion

This chapter investigates whether it is fundamentally possible to synthesize membranes based on plastic waste. It is found that the results of an exploratory study, performed in 2011, cannot be used as such because the methods to measure permeability and retention are not scientifically correct. However, the exploratory study allows to narrow down the options for five **production parameters**:

1. Material choice: post-consumer waste of PS, EPS and ABS is suitable for membrane synthesis. PC and PVC however, are not suitable because they are not sufficiently soluble in the solvent, NMP.
2. Polymer solution composition: 25 wt% of polymer gives the best tentative results. Therefore, 25 wt% is a good starting value for this thesis research. In the future, further investigation of the composition is important to optimize the membrane performance.
3. Membrane casting thickness: 250 µm leads to the least membrane defects.
4. Support layer: using a support layer (*e.g.* Novatexx 2471 PP/PE) reduces the brittleness of the membrane compared to using no support layer.
5. Coagulation medium: distilled water gives the best tentative results and is therefore used during this thesis research. In the future, further investigation may be important to optimize the membrane performance.

A validation of the experiments of the exploratory study shows that retention and permeability are overestimated in the exploratory study and establishes the reasons of these overestimations: transient effects, such as compaction of the membrane and initial adsorption of the dye on the membrane surface are not taken into account in the exploratory study. However, the experimental results of the validation are still reasonably high.

To evaluate the fundamental feasibility of the plastic waste derived membranes, experiments based on the dye congo red are conducted to compare with reference values for commercial NF membranes. These experiments show that one type of membranes (PS, based on CD-cases) have a performance comparable to commercial NF membranes. Two other types of membranes (EPS, based on single-use plates; and ABS, based on LEGO®) have a comparable PWP, but a slightly lower retention than the commercial NF membranes.

Chapter 5

Phase II: Scale-up

”What is the catch?”

”Plastic waste can be used to purify water in a cheaper way... What is the catch?” - this question is often posed by industry when reviewing the business plan for this technology. And they are right to be critical: using plastic waste most likely has effects on large-scale manufacturing of membranes, compared to using virgin plastics. These effects may not be identified during lab-scale membrane synthesis - when working with small volumes of plastic waste - but can be crucial for application at larger scale.

This chapter aims to answer their question. The first section identifies the possible negative (and positive) effects of using plastic waste when manufacturing membranes. Moreover, solutions are proposed to overcome negative effects. The second section further investigates a switch from post-consumer to post-industrial plastic waste, which is one of the most crucial proposed solutions of the first section.

5.1 Effects of using plastic waste

To identify the effects of plastic waste, two approaches are adopted. The first approach is to conduct interviews with experts in the plastic recycling industry. This allows to get a broad view on any technical, commercial and legal problems encountered by experienced players in the field. Interviews have been conducted with experts in different positions and companies:

1. Eric Goddaert, Managing Director Recycling at Indaver (a large Belgian waste management company);
2. Bart Vercauteren, Quality Controller at Indaver;
3. Amanda Latinne, Owner & General Manager at B&A Plastics and Plastics Latinne-Neyens (two Belgian SMEs in plastic recycling).

The second approach is to adopt a critical, forward-thinking mindset during the experimental lab work. The focus is on identifying issues which, though perhaps easily overcome at lab scale, can pose a problem once the manufacturing is scaled up.

Using both approaches, the following effects are identified:

1. Technical effects:
   a. Post-consumer plastic waste streams are **not consistent** but have a varying composition.
   b. Plastic waste can contain a variety of **additional components**.
   c. Plastic waste streams can be **contaminated**.
   d. Variable product shape can **limit automation**.
2. Commercial effects:
   a. Plastic waste is significantly **cheaper** than virgin plastic.
   b. Using plastic waste is **sustainable** and can be beneficial for a company's image.
   c. The **client-supplier relation** can often be difficult.
3. Legal effects:
   a. **Liability** for waste material composition.
   b. Safety **regulation** for water purification.

Each effect is discussed in detail in the following sections:

5.1.1 Technical effects of using plastic waste

a. Post-consumer plastic waste streams are not consistent but have a varying composition.

In the fundamental study, post-consumer plastic waste is used. Experts indicate that these waste streams are not consistent. They have a changing composition and a variable quality, which makes it difficult to use a certain waste stream continuously for membrane manufacturing, since the membrane quality varies accordingly.

This is also observed in the lab when working with CD-cases. Most commonly, CD-cases are made from polystyrene and represent a good resource for membrane manufacturing. However, some CD-cases are also made from other plastics, like for example PVC (see section C.1.2), which makes it impossible to manufacture membranes with the same solvent. Moreover, even for two polystyrene CD-cases there were significant differences between the different parts of the CD-case: the transparent top side and the opaque bottom of the CD case gave a different membrane performance.

To cope with this variability, the post-consumer plastic waste requires thorough screening and analysis before being accepted as resource for membrane manufacturing. It is clear that this causes post-consumer plastic waste to be impractical and expensive as resource.

There are two possible solutions for this problem. The first and most convenient solution is to select **post-industrial plastic waste**. This type of waste streams is typically very consistent. Besides, post-industrial plastic waste is attractive for the following reasons:

1. The post-industrial plastic waste market is more developed (higher availability, fixed pricing, and streamlined sales via intermediates like Indaver).
2. Post-industrial plastic waste usually requires less processing (only compression or cutting, no separation).

3. The volume prediction is straight-forward (can be estimated at the supplier level as a fixed percentage of the production capacity).

However, post-industrial plastic waste typically has a higher price compared to post-consumer plastic waste. The second solution is to work with high-purity post-consumer plastic waste collection. Since only small volumes of plastic waste are required for membrane manufacturing, high-purity waste collection is feasible. An example could be an Isomo® collection at the KU Leuven campus.

For this thesis research, the first option is chosen because it offers a wide choice of polymers and waste streams. The use of post-industrial plastic waste seems promising but its applicability should be further investigated. This is discussed in the section 5.2.

b. Plastic waste can contain a variety of additional components (fillers, plasticizers and other additives)

Plastics obtained from plastic waste (both post-consumer and post-industrial) are typically not pure. They can contain a variety of fillers, plasticizers and other additives in a variety of concentrations. These additional components can have an effect on the membrane performance. However, since post-industrial streams are very consistent, the effect is always the same and can be taken into account from the start: based on a sample of a post-industrial waste stream, it can be determined whether the stream - including additives - yields a sufficient membrane performance. If so, the stream can be used until the producer makes a change to the production line.

The additives can pose a problem when they leak out after dissolution of the polymer in the solvent. On a lab-scale, this leads to accumulation of the additives in the non-solvent bath. However, the non-solvent bath also accumulates solvent and lost polymer, so the bath must be replaced frequently anyway. Nevertheless, the resulting waste stream becomes more complex and may require a more special treatment because of the presence of the additives.

When scaling up the manufacturing, this issue can be taken into account in the design of the non-solvent bath. A solution could be to use a very small volume of non-solvent, leading to a small, highly concentrated waste stream to be handled. This can be implemented by for example spraying water over the film instead of submerging the film into a water bath. This should be further investigated when scaling up the production process.

c. Plastic waste streams can be contaminated

Plastic waste streams can be contaminated with other materials. This is especially true for post-consumer plastic waste which often contains food remainders, bacteria, incorrectly sorted materials, *etc.* For post-industrial plastic waste, this is typically less of an issue.

However, problems can arise if the partnership supplier-recycler is not correctly defined or acknowledged by the supplier (see commercial effect c). A potential issue arises from suppliers that regard the recycler as a total waste management company, leading to for example including non-production waste (*e.g.* promotion material) in the plastic waste stream. A correct partnership is the basis for solving such issues, and is discussed further (see commercial effect c).

d. Varying product shape can limit automation

The exact shape of products in the plastic waste stream can change, for example when the supplier makes a small change to its production line. This can present a limit on automating the recycling process (*e.g.* compressing or cutting steps). This problem can be solved by using an intermediate waste collection company (*e.g.* Indaver), that owns a variety of recycling machines capable of processing various shapes. On the other hand, the material does not require much processing for membrane manufacturing, since it is dissolved at the start of the membrane production process. A simple, coarse cutting process may be enough, and there are machines available that can do this for a variety of product shapes.

5.1.2 Commercial effects of using plastic waste

a. Plastic waste is significantly cheaper than virgin plastic

Plastic waste is significantly cheaper than corresponding virgin plastics. Producing virgin plastics comprises many steps, such as oil extraction, shipping, refining and polymerization. Plastic waste only requires collection, sorting and potentially a simple treatment step (*e.g.* cutting or compressing). Since plastic waste collection is in any case necessary for standard waste treatment, the additional cost for recycling plastic waste is very low.

However, for most pure, consistent post-industrial plastic waste streams, the price advantage is smaller than would be expected from this difference in production steps. This can be explained by supply & demand economics. For these pure, homogeneous waste streams, the demand is higher than the supply, leading to a supply-controlled market. This pushes up prices, reaching about 70%-75% of the prices of corresponding virgin plastics. The post-industrial plastic waste streams available at Indaver belong in this category.

However, some streams have a low demand, leading to a dramatic decrease in price. An example is EPS: because of its large air content (approximately 95% [43]) it has a very low packing density and is difficult to store and transport. As a result, the price of waste EPS can be as low as 1.25% of the virgin EPS price. This may be an interesting stream for membrane manufacturing, since the air content naturally leaves the plastic during dissolution, leading to an automatic compression of the volume. Other streams with low demand are impure or mixed streams, and waste streams from industries that have not yet found the way to a recycling application (*e.g.* a polyamide waste stream from the 3D printing industry). It may prove crucial to stay open for opportunities where these extremely low-cost waste streams can be valorized in membrane production.

One such opportunity, mixed waste streams, is tested by mixing a PS and ABS waste material (50/50 weight ratio). However, for this specific case, it proved to be impossible to cast a homogeneous membrane: a heterogeneous surface is obtained, where the polymer only provides partial coverage of the support layer, which results in a useless membrane. Despite this result, it is still interesting to identify and investigate other mixed streams, though this is beyond the scope of this research.

b. Using plastic waste is sustainable and can be beneficial for a company's image

The use of plastic waste as a resource is sustainable since (i) it increases reuse of plastic waste and (ii) it reduces the consumption of virgin plastics. In this way it contributes to a sustainable resource and waste management system. However, membranes are a low volume application of plastic resources. This means that changing the resource for this application to plastic waste, does not have a significant direct contribution to the sustainability of the planet.

However, the idea is still sustainable and can be used as such to change the perception of plastic waste in both industry and society:

1. Industry: promoting plastic waste as a resource for high-quality applications can help change the existing mindset in industry. The generally known principle of vertical integration with suppliers and customers is not yet applied to a company's waste management and their waste recyclers, leading to an often difficult client-supplier relation (see effect c). By introducing companies to high-end products that can be made from their waste, their waste management responsibility can be triggered and vertical integration can be expanded to a company's waste.
2. Society: tangible recycling projects can function as poster projects in the society to change people's thinking about plastic waste, and can help in sensitizing people about efficient collection and sorting of plastic waste.

Additionally, the use of products derived from plastic waste can be beneficial for a company's image.

c. The client-supplier relation can often be difficult

In the current industrial waste management and recycling landscape, the recycler is legally regarded as a waste management company. This means that legally the recycler is the supplier of a service to the industrial company producing the waste. This turns the actual supply chain around, because in reality it is the industrial company that is the supplier of waste to the recycler.

However, this has a consequence for the attitude of the industrial company towards the recycler. An often occurring problem is a disregard of the industrial company for the quality of its waste stream. Another issue is the supplier contracts, where the industrial company has the upper hand (as the client) and can set the contract terms and penalties.

There are two solutions to this problem. The first solution is to work with an intermediate (*e.g.* Indaver). This company delivers the waste management service, and sells the products to the recycler. This is the easiest solution, but of course incorporates extra costs.

Another solution is specific to the situation of membrane manufacturing. The problem described above is significant when working with a large number of industrial companies, which is usually the case when large volumes of plastic waste are required. For membrane manufacturing however, only small volumes are required. This means that the waste stream of one industrial company can be enough. When working with only one industrial company, it is much more convenient to screen the plastic waste stream for quality (and provide feedback), and it is easier to transform the negative client-supplier relation into a positive partnership.

5.1.3 Legal effects of using plastic waste

a. Liability for waste material composition

For virgin plastics, the responsibility for the quality of the plastics lies with the plastics supplier. Therefore, if any complication occurs, the supplier also bears the liability for possible material quality issues. For plastic waste, the situation is different. Like mentioned in section 5.1.2, the current legal landscape regards the recycler as providing a waste management service to the industrial company. Therefore, the responsibility of the material quality lies with the waste management company, not with the industrial company.

This can be solved in the same way as for the problem of the client-supplier relation: by working with an intermediate company (*e.g.* Indaver), that bears the liability of the products it sells. Another solution is to work with one industrial company, making a positive partnership and screening of the waste stream is much easier.

b. Safety regulation for water purification

When providing membranes for water purification purposes, the regulatory demands for membrane quality may be very strict. Generally, the REACH legislation applies for any new product and may imply an administrative burden [44]. When working with plastic waste as raw material, there may be additional regulatory demands to control the quality of the raw materials.

Although this quality control can be managed when working with one supplier in a partnership, it should be investigated to what extent these regulatory burdens may limit this new technology or introduce additional costs. This is however beyond the expertise of the author and is outside the scope for this thesis research.

5.2 Post-industrial plastic waste

In the fundamental study, post-consumer plastic waste is used for membrane synthesis. However, in section 5.1.1, it is found that post-consumer plastic waste has a varying composition, making it difficult to use such a waste stream continuously for membrane manufacturing, since the membrane quality varies accordingly.

To cope with this problem, the proposed solution is to use post-industrial plastic waste, which is typically very consistent. Post-industrial plastic waste is collected on a large scale in Belgium. A major waste collection company is Indaver, which has a plastic sorting site in Willebroek, Belgium. Following a visit to this site, fourteen post-industrial plastic waste streams (see section 3.2) are selected for further investigation and samples of each stream are kindly provided by Indaver.

These fourteen waste streams are candidates for a scalable membrane production. This section aims to narrow down this selection by analyzing their attractiveness for three important aspects of membrane manufacturing:

1. Operational: can the waste materials be processed in an efficient way?
2. Economic: which streams offer the highest financial incentive for recycling?
3. Membrane performance: can high-quality membranes be made?

Moreover, to obtain a research result that is more generally applicable than these specific waste streams, the membrane performance results are more fundamentally interpreted and investigated using SEM analysis. An approach toward generalizing the desired waste stream properties for membrane manufacturing is proposed and evaluated.

The first part of this section evaluates the plastic waste streams for the three aspects of membrane manufacturing. The second part interprets and further investigates the membrane performance results and proposes an approach toward generalizing the desired waste stream properties.

5.2.1 Evaluation of waste streams for membrane manufacturing

Operational factors

Important operational factors are the ease of processing of the waste material and the rate of dissolution in the solvent, NMP. Both factors strongly influence the production process: easy processing and quick dissolution lead to a shorter lead time and lower production costs.

The **ease of processing** is tested by trying to convert the waste material from its basic shape to small pieces of approximately 1 cm in size. The simplicity and speed of this process is rated for each material on a scale of 1 (most difficult) to 5 (easiest):

- 1/5: material requires use of specialized technical equipment (*e.g.* metal shear).
- 2/5 - 3/5: material requires use of standard technical equipment (*e.g.* cutting plier).
- 4/5: material requires use of simple scissors.
- 5/5: no processing needed (material is already in required shape and size, *e.g.* beads).

The **rate of dissolution** is tested by preparing a 30 wt% solution of each waste material in the solvent, NMP. The solution is stirred heavily and progress is observed. The speed of dissolution is rated for each material on a scale of 1 (insoluble) to 5 (easily soluble):

- 1/5: material is (partially) insoluble (even for 20 wt% solutions).
- 2/5: material requires more than 72 hours for complete dissolution.
- 3/5: material requires 72 hours for complete dissolution.
- 4/5: material requires 48 hours for complete dissolution.
- 5/5: material requires 24 hours or less for complete dissolution.

The results of these two analyses are summarized in table 5.1. A large number of materials are insoluble in the solvent NMP (shown in italics). Seven waste fractions are based on PA, PP, PE and PET; polymers which are intrinsically insoluble in NMP, so their insolubility was expected. The use of other solvents may solve this problem, though changing the solvent is out of the scope of this thesis research. The PS-C and PS-D waste streams, although identified as PS polymers by Indaver, are not soluble. DSC analysis (see appendix C) shows that these streams probably do not correspond to PS but to a different polymer or polymer blend.

The nine insoluble materials are not useful for this membrane production process and can be excluded from further investigation. A selection of five waste materials remains. These are further investigated in the following sections.

Table 5.1: Assessment of operational factors for post-industrial plastic waste streams

waste material	processability (1–5)	dissolvability (1–5)
PS-A	4	5
PS-B	3	4
PS-C	*1*	*1 (insoluble)*
PS-D	*2*	*1 (insoluble)*
PS-FR	2	4
ABS-A	3	4
ABS-B	1	2
PA	*5*	*1 (insoluble)*
PP-A	*3*	*1 (insoluble)*
PP-B	*4*	*1 (insoluble)*
PP-C	*4*	*1 (insoluble)*
PE-A	*4*	*1 (insoluble)*
PE-B	*5*	*1 (insoluble)*
PET	*3*	*1 (insoluble)*

Economic factors

Important economic factors are the material costs and the transport costs. These costs have major influence on the overall economic outlook of the new membranes.

The **material costs** are determined by prices Indaver demands for these materials. Indaver has provided cost data, but these absolute figures are not included in this report at the request of Indaver. Therefore, a relative scale from 1 to 5 is used, with the first material (PS-A) used as a reference material, given a score of 5 (most expensive). Related to material costs is also the volume of material that is collected and therefore available for purchase.

The **transport costs** are determined by two characteristics of the waste material. The most important characteristic is the density of the waste material. A high density results in a more efficient transport. The second characteristic is the shape of the waste material. Some shapes allow for easy stacking, and can again be more efficiently transported. Both characteristics are taken into account by assessing the weight per container, of which information is kindly provided by Indaver. Table 5.2 contains the evaluation of the three economic factors for the remaining five waste streams.

Table 5.2: Assessment of economic factors for post-industrial plastic waste streams

waste material	material cost (1–5)	product volumes [ton/year]	transport efficiency [ton/container]
PS-A	5	28	15
PS-B	5	28	15
PS-FR	<1	14	15
ABS-A	5	2.5	15
ABS-B	2.5	17	3

Membrane performance

A critical aspect is of course the membrane performance. The five remaining plastic waste streams are used to synthesize membranes using the immersion-precipitation method (see section 3.2). The membranes are tested for retention of an aqueous dye solution (congo red, 14 ppm) and for pure water permeability. Table 5.3 summarizes the results, and compares them to reference values for commercial NF membranes.

Table 5.3: Experimental performance of post-industrial plastic waste membranes for congo red compared to a selection of commercial NF membranes

waste material	retention [%]	pure water permeability $[L/m^2/h/bar]$
PS-A	89% – 94%	11 – 18
PS-B	84% – 92%	8.4 – 20
PS-FR	72% – 73%	49 – 153
ABS-A	69% – 88%	79 – 125
ABS-B	70% – 77%	94 – 115
Commercial NF	92% – 99%	3.0 – 25

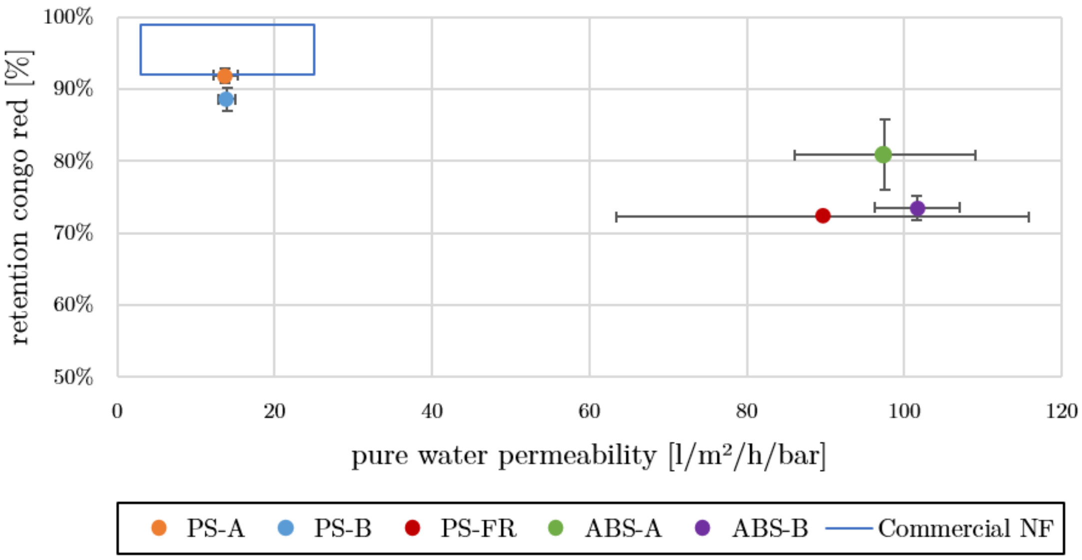

Figure 5.1: Experimental performance of post-industrial plastic waste membranes for congo red compared to a selection of commercial NF membranes

However, to allow for a good comparison, a graphical representation may be more suitable and is given in figure 5.1. Average values of the experimental results are plotted, and error bars indicate the standard error of the mean. The blue box in the upper left corner represents the range for the selection of commercial NF membranes. The interpretation of these results is not based on a simple linear scale, as was the case for the operational and economic factors. This is because there exists a trade-off, inherent to all membranes, of permeability and retention. Typically, membranes with a very high retention have a lower permeability and vice versa [22].

It is useful to identify groups of membranes with similar performance, and link these groups to specific applications. Based on figure 5.1, three groups of similar membranes can be identified: (i) PS-A and PS-B, (ii) PS-FR, and (iii) ABS-A and ABS-B.

The group of PS-A and PS-B membranes show a high retention (84% - 92%) and a relatively low permeability (8 - 20 L/m^2/h/bar). Compared to the range of retentions for commercial NF membranes, the retention of PS-A is on the lower edge of this range. The retention of PS-B is slightly below the commercial membranes. The permeability of PS-A and PS-B is comparable to the commercial membranes. These results show PS-A and PS-B membranes may be suitable for less demanding NF applications, where a >99% retention is not required. They may also be suitable to apply as a support layer for the preparation of thin-film composite (TFC) membranes. These applications are further discussed in the chapter 6.

PS-FR membranes have a much lower retention (71% - 73%) combined with a high permeability (49 - 153 L/m^2/h/bar). There is a high variability in the permeability. Further tests show that PS-FR membranes are prone to crack formation on the surface, which can lead to defects and strongly reduced retention. This characteristic may be caused by the presence of an additional fire retarding component in the polymer. Because of the strongly varying performance of PS-FR membranes, they do not seem very useful and are not further investigated in this thesis research.

The group of ABS-A and ABS-B membranes show a lower retention (69% - 88%) but a much higher permeability (79 - 125 L/m^2/h/bar) compared to the first group. They are very different from the commercial NF membranes. Their low retention shows they are not suitable for commercial NF. Interestingly though, their permeability is very high and these membranes may be successfully applied to retain somewhat larger compounds, for example in commercial UF or MF. These applications are further discussed and investigated in chapter 6.

5.2.2 Understanding of membrane performance

In this section, the aim is to more fundamentally understand the differences in membrane performance shown in figure 5.1.

In essence, the membrane performance depends on the specific **pore structure**. SEM (scanning electron microscopy) is an effective tool to visualize and investigate this pore structure. A SEM analysis is executed and details can be found in appendix D. The SEM images allow for a qualitative comparison between the pore structures of the different membranes on two main aspects:

1. Sublayer structure: sponge-like or finger-like structure and presence or absence of macrovoids.
2. Top layer thickness.

The first aspect contains information about the permeability of the membrane, the second aspect about the retention of the membrane. A finger-like structure is characterized by long finger-like channels in the sublayer of the membrane. A sponge-like structure looks similar to a finger-like structure, however the walls between the different fingers are perforated. This leads to a better connectivity of the finger-like channels and therefore a higher permeability. Sponge-like membranes are therefore typically associated with higher permeabilities. Macrovoids are large elongated voids, and are also associated with higher permeabilities. [22,45,46]

The second aspect, the top layer, is a thin layer at the surface of the membrane. This layer has the smallest pores of the membrane, and is therefore essential in determining the retention of the membrane. A thick top layer means it is more difficult for solutes to pass the membrane. Therefore, a thick top layer is associated with a higher retention. [22,46]

SEM images indicate that the PS-A and PS-B membranes have a typical asymmetric structure consisting of a thin top layer with a porous finger-like sublayer. The top layer is relatively thick ($> 1\,\mu m$). The PS-FR membranes also have finger structures, but these are more perforated with additional pores, which is leaning towards a sponge structure. The top layer thickness of the PS-FR membranes seems to be smaller ($< 1\,\mu m$). Similarly, the ABS-A and ABS-B membranes also have perforated finger structures, and seem to have a small top layer thickness ($< 1\,\mu m$). They also seem to contain more macrovoids than the PS-A and PS-B membranes. More information on the SEM images can be found in appendix D.

These findings correspond to the earlier experimental observations, *i.e.* that PS-A and PS-B membranes have a higher retention and a lower permeability compared to the PS-FR, ABS-A and ABS-B membranes.

The exact mechanism behind the differences in pore structures should be sought in thermodynamic and kinetic differences, since both are important during the phase inversion process, as explained in section 2.2.2. This requires more fundamental research and is out of the scope of this thesis. However, a pragmatic investigation of the parameters mostly influencing this pore structure - and ultimately, the membrane performance - is worthwhile.

Generalization of desired waste stream characteristics

Even without knowing the exact fundamental effects on the pore forming mechanism, we may be able to relate the differences in membrane performance to differing material characteristics of the waste streams. This section aims to determine the essential properties in a waste stream that control the membrane performance. This allows to expand the discussion of five specific waste streams to a **general** discussion on waste stream characteristics important for membrane manufacturing. **Ideally, a waste stream could be evaluated for membrane manufacturing based on testing a few characteristics, allowing for an easy selection of potential waste streams.**

In this section, two waste stream characteristics are investigated: the chemical composition of the polymer and the viscosity of the polymer solution.

Chemical composition of the polymer. In section 5.2.1, membranes with similar performances are grouped based on figure 5.1. These groups correspond to the chemical composition of the polymer material. Consequently, the chemical composition seems to be the most important characteristic. The polymer PS results in high retention and low permeability. Additional components (fillers, additivies, *etc.*) may be important. The case of PS-FR (containing a fire retarding component) leads to crack formation and therefore useless membranes. The polymer ABS is a terpolymer also containing styrene. The presence of the other monomer units (acrylonitrile and butadiene) results in lower retention but higher permeability.

The effect of the chemical composition of the polymer on membrane performance can be related to thermodynamic effects in the pore formation. Most likely, the Gibbs phase triangle of the PS-NMP-water system differs from that of the ABS-NMP-water system. For example, a small difference in the positions of the binodal and spinodal curves can lead to a different phase separation mechanism and therefore a different pore structure.

In this light, when selecting new waste streams for membrane manufacturing, the chemical composition of the polymer waste should be identified. Based on this research, PS and ABS are found to be good options. However, the composition is often not known beforehand. The polymer type can be unknown or incorrectly specified by the supplier; the polymer can also contain fillers and additives. To rectify this, an analysis method is necessary.

In this study, differential scanning calorimetry (DSC) is used to analyze the chemical composition. DSC can determine the thermal behavior of the different samples, giving an idea of their chemical composition [47, 48]. In fact, IR spectroscopy would be a more decisive technique for this [49], but was omitted due to practical reasons. Other parameters, such as the identity of the fillers or the quantity of the fillers, can also be important. They can be analyzed using IR-spectroscopy (identity of fillers) and thermal gravimetric analysis (quantity of fillers).

The PS and ABS post-industrial waste materials are analyzed using DSC. The analysis, which is included in appendix C, shows that samples PS-A, PS-B and PS-FR are most likely polystyrene. However, it is possible that PS-B and PS-FR contain impurities. The samples PS-C and PS-D do not seem to correspond to polystyrene; PS-C is more similar to polycarbonate, while PS-D seems to be a blend of polystyrene and a crystalline polymer like polyethylene. This can explain why samples PS-C and PS-D do not dissolve in the solvent, NMP. The samples ABS-A and ABS-B seem to correspond to the polymer ABS. However, the material from ABS-B is covered with a film. Since this film does not correspond to ABS, it should be removed before membrane manufacturing.

Viscosity of the polymer solution. There are also differences between membranes of the same polymer type (PS-A vs. PS-B and ABS-A vs. ABS-B). A polymer characteristic that may be responsible for these differences, is the viscosity. This can be different when for example the molecular weights of the polymers are different.

It is presumed that the viscosity is important, since it influences the kinetics of the phase inversion process, and therefore influences the pore size and structure. Based on the pore formation of the phase inversion process (see section 2.2.2), a positive correlation is expected between viscosity and permeability. The hypothesis is that a high viscosity leads to a more difficult exchange of solvent and non-solvent in the polymer film, causing slower entry of non-solvent in the sublayer during the phase inversion process. This leads to a lower degree of supersaturation in the sublayer, and therefore a slower precipitation from fewer nuclei, and a longer time between precipitation and solidification. This results in a coarser pore structure of the sublayer, leading to a higher permeability. [37]

To test this hypothesis, the viscosity is evaluated for the different waste materials and this is compared to the differences in membrane performance.

To determine the viscosity of a polymer, different techniques can be used. Here, rheometry is chosen to determine the viscosity of the polymer melt. In reality, it may be more accurate to determine the viscosity of the polymer in solution (which is how it is present during phase inversion), for example by using viscometry. However, the objective is only to perform a qualitative analysis: we want to see whether a difference in membrane performance corresponds to a difference in viscosities. Moreover, both melt and solution viscosity of a polymer are highly dependent on its molecular weight [49]. Hence, they can often be related. Therefore, rheometry suffices[1] and is chosen because it was more conveniently available.

The details of the rheometry analysis are included in appendix D. The analysis shows that the viscosity of PS-A is higher than that of PS-B. This does not correspond with a difference in membrane permeability, because the permeabilities of PS-A and PS-B membranes are similar (see figure 5.1). For the ABS-A and ABS-B polymers, rheometry shows the viscosities are similar. This seems to correspond with the observation that (when taking into account the standard errors) there is no significant difference between the permeabilities of both ABS membranes (see figure 5.1).

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[1] More information about why rheometry suffices is given in appendix D.

Based on this limited analysis of four materials, no conclusions can be made on the importance of viscosity for the membrane performance. However, the data do not seem to comply with the hypothesis: viscosity does not seem to be the main determining factor regarding the membrane performance of materials of the same polymer type. This difference between hypothesis and experiments can be explained in a number of ways:

1. Other effects are dominating: other characteristics may be more important than the viscosity difference (*e.g.* the presence of unknown additives). This can be investigated by performing a more detailed analysis of the chemical composition (*e.g.* by IR spectroscopy), which is beyond the scope of this thesis research.

2. Incorrect hypothesis: the viscosity may enter in a more complex way in the phase inversion process or the relationship between solvent and non-solvent kinetics and polymer viscosity may be oversimplified.

3. Incorrect viscosity measurement: the melt viscosity can give an incorrect image of the viscosity during the phase inversion process (in solution). For example, the presence of plasticizers can lower the melt viscosity, but since they are lost in solution, do not influence the solution viscosity. This can be investigated by performing a viscometry analysis instead of a rheometry analysis.

To be able to generalize the desired properties of a waste stream for membrane manufacturing, it is interesting to further investigate the effect of viscosity, and other characteristics, on membrane performance, though this is beyond the scope of this thesis research.

5.3 Conclusion

The use of plastic waste instead of virgin plastics has important effects on a technical, commercial and legal level. Based on expert interviews and insights from lab experiments, nine effects have been identified and solutions for most of them have been suggested. Especially on technical and commercial level, the negative effects can be overcome and positive effects can provide significant advantages. On legal level however, the effects can burden the application of this technology. Specifically the additional regulations concerning the use of plastic waste in membranes should be further investigated.

Of course, it is difficult to see all the effects plastic waste can have at this stage. Pilot scale experiments are crucial to identify other issues of plastic waste and to start working on solutions.

The most prominent technical problem is the inconsistency of post-consumer waste, leading to a variable membrane quality. The proposed solution is the use of more consistent post-industrial waste. This solution is investigated in more detail. Fourteen post-industrial waste streams are selected and investigated for membrane production on an operational, economic and membrane performance level. In the end, four materials (PS-A, PS-B, ABS-A and ABS-B) are found to have potential for commercial membrane filtration. Chapter 6 continues with these four materials to further investigate their applicability.

Based on the experimental membrane performance and SEM analysis of these four materials, a more detailed understanding of the reasons behind a certain membrane performance is gained. It is found that the chemical composition (polymer type and presence of additives) of the waste stream is crucial. A DSC analysis can be a useful tool in screening waste streams for their chemical composition. Also another waste stream characteristic, the polymer viscosity, is investigated: although a positive effect of viscosity on permeability is expected from theory, no direct relation is observed.

Chapter 6

Phase III: Application

"Is the technology competitive for industrial applications?"

The previous chapters show that (i) membranes can be made from plastic waste and (ii) post-industrial plastic waste membranes can possibly be applied at large scale. However, to bring this technology to application in industry, it is also necessary to evaluate the industrial applicability of the technology. This chapter aims to assess whether the technology is competitive - both technically and economically - for industrial applications.

The first section of this chapter investigates the technical competitiveness. Based on the results of chapter 5, two groups of membranes are identified. For each group, potential applications are identified and evaluated. The second section uses the results of the first section to evaluate the overall business potential of the technology, and sets the ground for a potential university spin-off to commercialize the new membrane technology.

6.1 Applications

This section continues with the two successful groups of membranes (PS-A and PS-B ; ABS-A and ABS-B) identified in the previous chapter. Based on their membrane performance data, potential applications are identified. These applications are further investigated in this chapter.

6.1.1 Group 1: PS based membranes

The PS-A and PS-B membranes combine a relatively high retention (84% - 92%) with a relatively low permeability (8 - 20 L/m^2/h/bar) (see section 5.2). This is comparable to commercial NF, though with a slightly lower retention. This may indicate that these membranes are more suited for **less demanding NF applications**, where a >99% retention is not required. This could be the first step in a hybrid separation: the PS-A or PS-B membranes could provide a more cost-efficient separation of an already large fraction of the solutes, followed by a more expensive, but less intensively used polishing step.

The PS-A membranes have a slightly higher retention and a similar permeability compared to the PS-B membranes. The economic and operational analysis shows that the PS-A materials are easier to process and have similar costs. Based on these factors, the PS-A membranes show most potential, though the difference with PS-B is small. To further investigate this application, the membranes can be tested for a variety of solutes in the range of NF.

The PS-A and PS-B membranes may also be suitable to use as a support layer for the preparation of **thin-film composite (TFC) membranes**. TFC membranes are composed of a thin top layer, typically made of polyamide or polyimide; which is coated over a porous support membrane. TFC membranes - combining a dense top layer with a porous substructure - have an asymmetric structure to achieve higher retention while keeping a high permeability. TFC membranes can be used for high-quality NF applications in desalination, freshwater softening, removal of organics, ultrapure water production and advanced wastewater purification. [45]

An important requirement for the porous support layer is that it has a narrow pore surface structure, to form a stable base for the top layer coating. If the pores on the surface are too wide, the top layer collapses during its synthesis and enters the pores, causing blocking of the pores and the formation of an irregular top layer [45]. Based on the experimental results for the retention of the membranes (see section 5.2), the PS-A and PS-B membranes have a retention that indicates they may be suitable for TFC membranes. Their lower permeability is less important for this application, since the rate determining barrier is typically the top layer and not the substructure [45, 46]. Based on the membrane performance, operational and economic factors, the PS-A membranes have slightly more potential than the PS-B membranes. To investigate this application, it is necessary to explore the synthesis of a top layer on the PS-A and PS-B membranes, which is beyond the scope of this thesis research.

6.1.2 Group 2: ABS based membranes

The ABS-A and ABS-B membranes have a lower retention (69% - 88%) but a very high permeability (79 - 125 $L/m^2/h/bar$) (see section 5.2). An application should be selected with solutes larger than the dyes tested previously, in order to valorize the high permeability. The hypothesis is that for solutes in the range of MF or UF, a high retention (>99%) can be achieved, combined with the high permeability tested already.

The experimental results of section 5.2 are not sufficient to assess the application of MF and UF. Therefore, to test the hypothesis, dead-end tests have been conducted with feed solutions typical for MF and UF. These are discussed in the following sections.

MF application

To evaluate the ABS-A and ABS-B membranes for microfiltration, they are tested for retention of an aqueous solution (100 ppm) of fluorescent polystyrene beads of 1.0 µm mean particle size. This particle size fits in the range for MF (100 nm - 10 µm) and is used to represent a typical MF feed solution.

The results for retention of the particle solution and pure water permeability are summarized in table 6.1. The membranes obtain a very high retention, which is beyond the detection limit of the analysis equipment (the accuracy of the UV-spectrophotometer is in this case limited to 99.5% retention).

The pure water permeability is tested again, but is in fact already tested in section 5.2. For the ABS-A membranes, the pure water permeability is lower now compared to the previous experimental results of section 5.2 (80 - 120 L/m^2/h/bar). This is because the membrane production process is slightly updated[1] after synthesis of the ABS-A membranes of section 5.2. The ABS-B membranes of section 5.2 are already synthesized with the updated process, and therefore correspond to the results of table 6.1.

These results can be compared to commercial MF membranes. Commercial membranes typically reach retentions of (practically) 100%, combined with a permeability of 500 - 5,000 L/m^2/h/bar [10]. This permeability is much higher than the permeability obtained by ABS-A and ABS-B. This shows that most likely the pore size of the membranes is too small to apply in microfiltration. There may be more potential for these membranes for filtrating smaller solutes, for example in ultrafiltration.

TABLE 6.1: Experimental performance of post-industrial ABS waste membranes for beads (1 µm) compared to commercial MF membranes

waste material	retention [%]	pure water permeability $[L/m^2/h/bar]$
ABS-A	>99.5%	46 – 53
ABS-B	>99.5%	79 – 112
Commercial MF	100%	500 – 5,000

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[1] The most important process change is to keep the membranes for 60 minutes instead of 15 minutes in the non-solvent bath after synthesis, and, after a quick rinse, for another 24 hours in a second water bath, instead of immediate cutting and conservation.

UF application

As UF feed solution, an aqueous solution (500 ppm) of 30 nm mean particle size fluorescent polystyrene beads is used. This particle size fits in the range for UF (10 nm - 100 nm) and is used to represent a typical UF feed solution.

The experimental results, provided in table 6.2, show that the ABS-A and ABS-B membranes have a very high retention (beyond the 99.5% detection limit of the analysis equipment), combined with a high permeability (46 - 86 L/m^2/h/bar). To compare with commercial UF membranes, no specific data on filtration with these fluorescent polystyrene beads is available, though it can be assumed that a qualified membrane can retain approximately 100% of the beads. An average value for the permeability of commercial UF membranes is considered to be 50 L/m^2/h/bar [10], though there is a large variety in commercial membranes (*e.g.* depending on the solute size). These ABS-A and ABS-B membranes score very well compared to the commercial UF membranes, meaning they have **much potential for high-quality commercial UF**.

On average, the permeability of the ABS-B membranes is higher than that of the ABS-A membranes. The analyses of the previous chapter show that the ABS-B material costs are significantly lower but that the ABS-A materials are easier to process. Based on these three factors, the ABS-B membranes show most potential.

To further investigate the membranes for this application, they can be tested for a variety of solutes in the range of UF.

Table 6.2: Experimental performance of post-industrial ABS waste membranes for beads (30 nm) compared to commercial UF membranes

waste material	retention [%]	pure water permeability [$L/m^2/h/bar$]
ABS-A	>99.5%	46 – 59
ABS-B	>99.5%	52 – 86
Commercial UF	100%	$< 50 >$

6.2 Business potential

6.2.1 Motivation

This section builds upon the results of the previous chapters, and aims to **investigate the business potential of the technology**.

Often, in academic literature, the business potential of a new technology is assessed by performing a cost analysis: comparing the investment and operational costs of the new technology with conventional techniques. However, after this cost analysis, the academic researcher usually does not actively pursue application of his technology. This finds its origin in a traditional separation between university and the for-profit sector. This mindset - though leading to many publications - includes that much academic work is not further pursued and applied. Whereas in reality, successful application of a technology is attractive for the academic community, since commercial success leads to societal impact, beyond knowledge creation and publication. [50]

Most university-produced technologies need significant additional development to commercialize them successfully. Therefore, to push successful academic research to increased industrial application, it is found critical to **involve the researcher in the commercialization** process [50]. Therefore, to increase application of academic research it is necessary to disrupt traditional lines between university and the for-profit sector, and have the researcher pursue the business side of the new technology, beyond a traditional cost analysis. Academic entrepreneurship embodies this reasoning: by means of **university spin-offs**, researchers can commercialize their technology. [51]

In light of this challenge, a more elaborate analysis of the business potential of a new technology is required, which simultaneously sets the ground for a university spin-off. To achieve this, the researcher should regard the new technology within a complete **business model**. Such a business model transforms an abstract technological concept to a concrete business set-up by finding real suppliers, real competitors, and real customers. Based on this business model, the researcher can investigate how the new technology can be applied in the actual industrial landscape and how all stakeholders interact with it. This is useful since the business potential of any new technology depends on more than costs: it depends on establishing new supplier relations, on interrupting loyal customer's relations, on developing the right marketing strategy, on finding a feasible sales approach, and more.

To adopt this strategy, the methodology proposed - and applied - in this thesis research consists of two steps:

1. Develop a business model for the new technology from a spin-off perspective.
2. Analyze the feasibility of this business model, by looking more closely at:
    a. Industry & market feasibility
    b. Product feasibility
    c. Financial feasibility

This approach can reveal whether it makes sense to develop the technology on an industrial level.

6.2.2 Business model

Context

Water - its scarcity, quality and regulations - is becoming a new corporate concern. In almost two-thirds of the world's largest companies water is or will soon become a constraint on their growth [52]. Also, industry in high-income countries is open to new green technology because of a variety of factors: widespread adoption of the sustainability concept, growing awareness of climate change, socioeconomic pressures, and the development of new technologies [9]. However, a green technology must be competitive to existing technologies.

To commercialize this technology, the proposed venture is a university spin-off, called **GreenWater**. One type of membranes, the UF membranes derived from post-industrial ABS waste, is chosen as product. In developing the business model, a distinction is drawn between high-income countries and low-income countries, since the market needs and industrial context are completely different. This research focuses on industry in high-income countries. Low-income countries require a specific approach which is discussed in [39, 53].

In the following sections, a business model is developed. First, the business opportunity is sketched. Secondly, it is described how GreenWater should act upon this opportunity by explaining the complete supply chain. Finally, the intellectual property strategy is defined.

Business opportunity

The business opportunity is explained by (i) defining the market, (ii) indicating the market needs, and (iii) explaining the market structure and choosing the direct customers.

Market definition. Three large potential markets are suitable for GreenWater:

1. **Industry:** many industrial companies have an expensive water supply, but on the other hand also require extensive treatment to discharge their wastewater. Conventional water sources are becoming increasingly expensive and environmental wastewater regulations are becoming stricter. This forces industry to expand their water treatment and reuse the treated wastewater (*i.e.* internal water recycling). Companies are looking for a cost-effective and ecologically responsible way to do this.
2. **Households:** the demand for residential water treatment is increasing. Households want a reduction in their water bill by cost-effective reuse of water and prefer that this happens in an ecological way.
3. **NGOs:** NGOs, active in third-world countries, are often confronted with regions where more than 50% of the population does not have access to clean water [54]. There is an obvious demand for cost-effective, simple, and environmentally sustainable water treatment systems.

All three markets can be addressed. In the first stage, GreenWater focuses on industry: industrial players have the largest incentive for water management, are more easily accessible, and are financially stronger to support investments.

The product of GreenWater is applicable for UF. UF applications include removal of particulates, bacteria, viruses, and natural organic matter from surface water, wastewater, and industrial water supplies; or pretreatment for reverse osmosis [13, 29]. Therefore, target industries include water, (petro-)chemical, pharmaceutical, food & beverage, paper and semiconductor industries [34].

In a further stage, GreenWater can approach other industries (*e.g.* building contractors for large apartment blocks), the residential market and the NGO market.

Market needs. Industrial companies invest in a water treatment system for economic, operational and legal reasons:

1. Internal water recycling is an additional and reliable source of water, which can complement or replace existing sources, leading to a reduced intake of water
2. Reduced production of waste
3. Complying to environmental regulations
4. No need to apply for permits for water use

Ideally, they require a reliable installation that, without much maintenance and control, can treat a certain volume of wastewater and produce water of a certain quality to reuse in their process. However, there are currently two major issues in industrial water treatment:

1. **Costs:** water treatment installations represent a significant investment. This is currently one of the main reasons why many (mostly smaller, less financially strong) companies do not invest in internal water recycling. The membrane cost is estimated at 25% of the total investment cost [55], and membrane replacement costs are recurring costs. For these reasons, the membrane cost represents a major decision factor for investment decisions.

2. **Green image:** internal water recycling is often associated with sustainable corporate behavior. However, the use of less ecological water treatment methods (*e.g.* filtration with active carbon) can undermine this image, and may diminish corporate efforts.

Market structure. The market is structured in the following way (see figure 6.1): membrane suppliers provide membranes for OEMs (original equipment manufacturers), which install a complete water treatment system for the end user. The market of end users consists of industrial companies active in various sectors.

The OEMs are chosen as direct customers. GreenWater supplies membranes to the OEM and can offer a service for the use of the membranes and potentially for the recycling of the membranes after use. The choice for OEMs as direct customers, instead of supplying directly to the end-users, is based on a low acquisition cost vs. customer lifetime value ratio of OEMs, as will be explained in the first part of section 6.2.3.

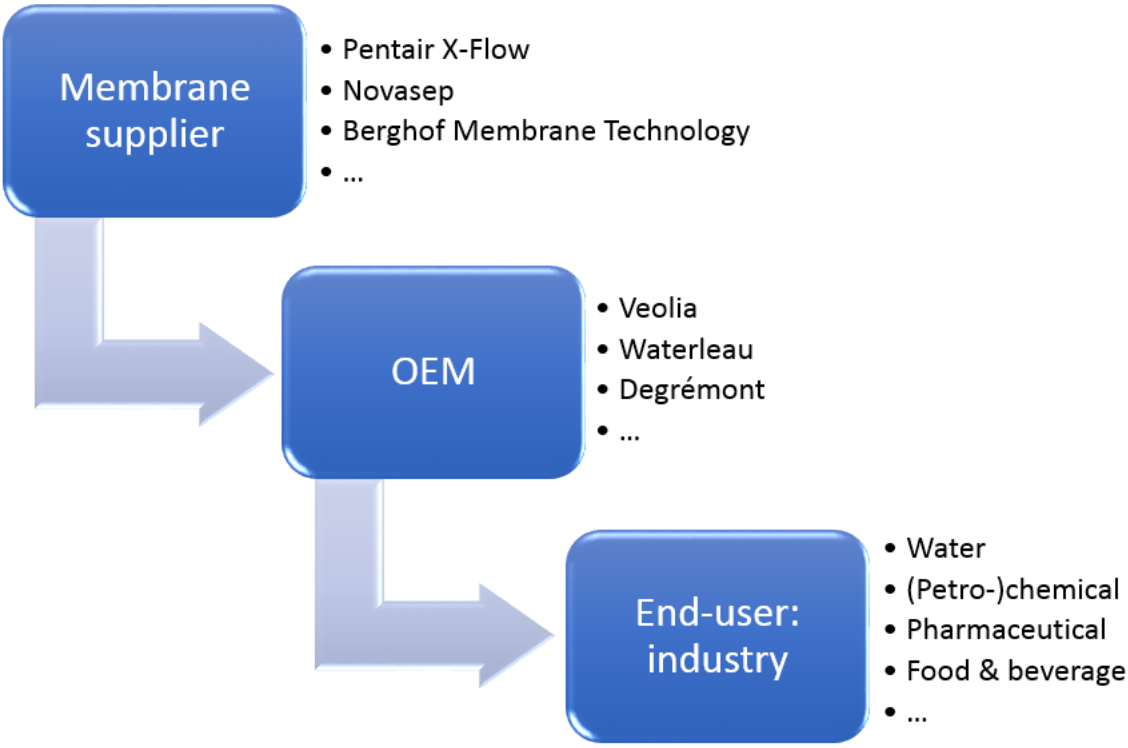


FIGURE 6.1: Simplified market structure

Supply chain

GreenWater positions itself in the market as a membrane supplier. The industry supply chain - containing GreenWater - is shown in figure 6.2, and contains the following market players:

1. **Plastic waste suppliers:** The most important raw material is plastic waste. As discussed in chapter 4, either post-industrial plastic waste or high-purity post-consumer plastic waste can be used.
   The most convenient suppliers of post-industrial plastic waste are local sorting centers. Various companies are active in this market in Belgium (Indaver, Valtris, Aive, Imog, Sita, Sitel, Valodec, Vanheede, Van Gansewinkel, Recyclis, *etc.*).
   Alternatively, it may be interesting to skip the sorting center and go straight to the producer of the waste. This approach reduces costs (no profit margin for the sorting center), offers less opportunity for contamination with other waste streams (waste is received directly from the source), and maintains a direct communicative link with the producer of the waste (useful if for example a small change is made to the product composition).
   High-purity post-consumer plastic waste can for example be obtained in cooperation with KU Leuven. Even today, at the Department of Chemical Engineering of KU Leuven, high-purity EPS waste is collected.

2. **OEMs:** The direct customers of GreenWater are OEMs. These OEMs provide a full installation for the end-user. To do this, among other things, they have to purchase membranes. Well-known OEMs in this market are Veolia, Waterleau and Degrémont. A list of OEMs is provided in appendix E.

3. **Competitors:** Other membrane suppliers that can compete with GreenWater are for example Pentair X-Flow, Novasep and Berghof Membrane Technology. A list of membrane suppliers is provided in appendix E.

4. **End-users:** End-users for internal water recycling or water treatment considered here are industrial companies. The end-user makes an investment in an installation, and pays for recurring costs including membrane replacement, energy and maintenance. Important industries are water, (petro-)chemical, pharmaceutical and food & beverages.

5. **Consultants:** This market does not have a simple line structure from supplier to end-user. There are many different market players (*e.g.* energy audits, engineering consultants) playing an important role in the market.

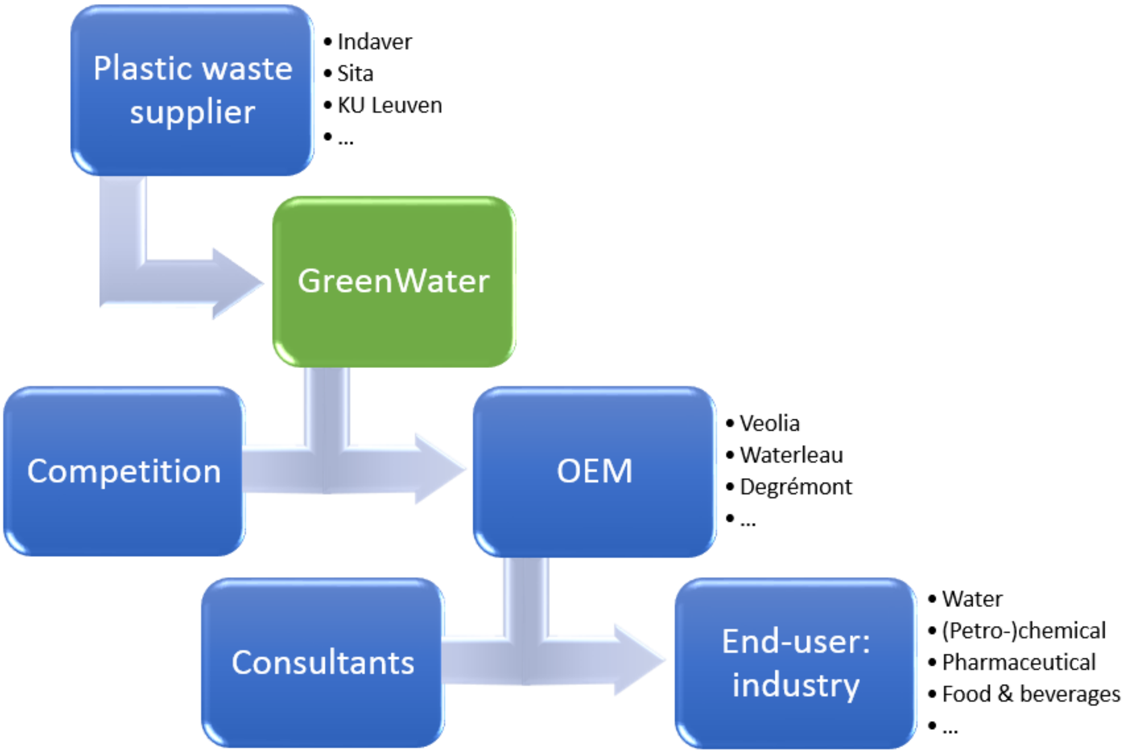


FIGURE 6.2: Industry supply chain

Potential partnerships along the supply chain. Partnerships are essential in the start-up of a new venture, for two reasons: GreenWater (i) does not have the resources to perform all the tasks required to make the business work and (ii) the majority of tasks needed to build a product are not core to its competitive advantage [56]. Therefore, it is crucial to look for potential partnerships along the supply chain. Three potential partnerships are identified:

1. **Membrane module producers:** A membrane is always contained in a module. Typically, the OEM purchases modules from a membrane module producer and inserts the membrane sheets or immediately purchases a module containing a membrane. The design of these modules is not yet investigated in our group at KU Leuven, and represents a gap in our expertise. A partnership with a membrane module producer (e.g. Pervatech) is interesting. GreenWater can partner up with one module producer to produce a module containing a membrane of GreenWater, which is then sold as a package. This partnership has the following advantages:

   a. Gain access to its existing customer base
   b. Risk and cost sharing
   c. Gain economies of scale
   d. Learn from their expertise in module design

   On the other hand, there are important risks of losing proprietary information and becoming dependent, so it is crucial to identify the right partner and to protect GreenWater from these risks via the partnership structure.

2. **OEMs:** It may be interesting to set up a partnership with an existing OEM, by for example having the OEM invest in GreenWater to become a shareholder. Advantages for GreenWater are an immediate customer base (which is crucial at the start of a venture) and the transfer of expertise and market knowledge from the OEM. For the OEM a partnership can give the advantages of vertical integration (*e.g.* increased efficiency and reduced costs) and can represent an interesting investment.

3. **End-users:** A major advantage of GreenWater's product is the underlying sustainability concept. However, this is - for typical end-users (industrial companies) - not a major selling point, because even if they use sustainable membranes, it is difficult to present this to their customers or employees as sustainable because they simply buy something sustainable - and are not necessarily sustainable themselves.
   An idea to valorize the sustainability concept of the product is to partner up with the end-user in the following way: the end-user collects and sorts his own plastic waste, GreenWater uses this plastic waste to produce membranes, and the end-user uses these membranes in their water treatment installation. This concept engages employees in sorting and recycling and functions as a poster project to show a sustainable waste management and water treatment system at their company. This is attractive for end-users, because they are reflected as a sustainable company towards their employees, and can also use this concept to improve their public relations.

Intellectual property

Patenting or not? The intellectual property is limited to the precise composition of the membranes and the gained insights in plastic waste. A general strategy is to patent the composition. However, it is important to be careful: patenting can surpass its goal to protect the idea, by making all the information public during the patenting procedure. This is essential, since a small change to the composition can make the patent useless.

For this reason, **keeping a trade secret protected by an i-DEPOT** can be a good choice. An i-DEPOT is a governmental registration that stays secret, but provides legal protection against potential future patents of competitors. Interestingly, it only costs € 35 for five years - extremely low compared to patent costs. [57]

6.2.3 Feasibility analysis

Now that a specific business model is proposed, the overall feasibility of this business model can be evaluated. This approach presents two advantages:

1. It is a more elaborate approach for estimating the business potential of a new technology than a traditional cost analysis, since it takes **all the business factors** into account, instead of only costs.
2. By analyzing the feasibility of the business model, the weak spots can be identified and a basis is prepared for a potential corporate strategy. This represents a **good foundation for a potential spin-off** later on.

In the following sections, the feasibility of the business model is assessed from three perspectives:

1. Industry & market feasibility: the market place of competitors and customers.
2. Product feasibility: the attractiveness of the product toward the customers.
3. Financial feasibility: the economics of the business model.

To perform consistent calculations concerning the feasibility, a spreadsheet-based **integrated economic model** is developed. More details about the contents of the economic model can be found in appendix F.

Perspective I: Industry & market feasibility

To assess the industry & market feasibility, this section consists of four parts: parts I.1 and I.2 analyze the attractiveness of the membrane industry and the water & wastewater treatment market, part I.3 explains the proposed market position and calculates its feasibility, and finally part I.4 explores future market expansion opportunities.

I.1: Industry attractiveness The industry in which GreenWater aims to compete is, generally speaking, the membrane industry. An industry analysis (see appendix E) has been conducted. This industry analysis contains a description of the membrane industry, a list of companies active in it (*i.e.* the competitors of GreenWater), and a price benchmark for comparable UF membranes. The highlights of the study are discussed here.

Table 6.3 summarizes key figures (of the year 2000) that quantify the global membrane industry [23, 25]. Globally, the membrane industry is rather consolidated with five global membrane suppliers having a combined market share of 91% in 2010 [6]. However, the rapid growth of the industry is attracting more and more smaller companies.

Table 6.3: Key economic figures of the global membrane industry

total turnover	€ 20 billion
sales of membranes and modules	€ 5 billion (25%)
annual growth	8% – 10%
UF & MF industry turnover	€ 1.4 billion

Locally, the membrane industry is very attractive. The size and large growth of the industry make it very attractive for new players, while locally very few players exist: there are no large players in Belgium and relatively little players in the rest of Europe, making market entry more convenient and local competition less intense.

However, when growing towards the global market, the high global consolidation of the membrane industry may cause increased competition and more difficult growth. A good approach may be a multi-domestic strategy: compete for market share on a country-by-country basis by varying the offering to meet the demands of each local market, instead of (too) quickly entering the global stage.

I.2: Market attractiveness Very broadly speaking, the customer market of GreenWater is the water & wastewater treatment (W&WWT) industry. A market analysis has been conducted (see appendix E). This market analysis contains a description of the W&WWT industry, and a description and list of the direct customers of GreenWater (the OEMs). The highlights of the study are discussed here.

Table 6.4 summarizes the key figures (of 2010) that quantify the global W&WWT industry [6]. The W&WWT industry consists of a small number of large OEMs (*e.g.* ITT and Siemens). Besides these large, global companies, there are many smaller, more locally active companies. [6]

TABLE 6.4: Key economic figures of the global W&WWT industry

total turnover	€ 283 billion
EU turnover	€ 94.5 billion
annual growth	0.7%
largest application	drinking water production (43% of treated water usage)

The W&WWT industry is a large, mature industry with a steady growth. Consequentially, there are some market barriers that obstruct new technologies. A reluctance of end-users to adopt new and unproven technologies, a lack of certification for new technologies, and a disconnect between industry and regulator knowledge cause increased risks for new companies wishing to bring unproven technologies to the market. Therefore, many processes have remained essentially unchanged for decades [6]. **This makes the market unattractive for new players.**

However, innovation and changes are currently occurring in membrane filtration and disinfection. This means the **industry is ready for innovation in membrane technology**: pioneering work has already been done (which is most crucial in convincing risk-averse companies), but there is still a lot of room for growth. In 2010, membrane filtration accounted for only 1.4% of the total industry [6]. Today, this presents an attractive opportunity for new players in membrane filtration.

I.3: Market position The market structure can be simplified to a linear structure (membrane supplier - OEM - end user), as shown before in figure 6.1. Some membrane companies choose to supply membranes directly to industrial end users. This has the advantage of higher margins (no profit margin for the OEM). However, for GreenWater the OEMs are chosen as direct customers, because of two main advantages:

1. OEMs already have an **existing customer base**. One sales contract with an OEM means access to a relatively large number of end-users. This means that OEMs have a high customer lifetime value (see further).
2. The **OEM market is highly consolidated**. A relatively small number of OEMs controls a large number of end-users. This is very interesting for a new venture, because sales and marketing efforts can be focused on a small number of OEMs. This means that the sales acquisition costs are low (see further).

These advantages are crucial for a new venture, since initially an active sales force is expensive. Focusing sales efforts on a smaller, more consolidated market is possible with a small sales force.

Often, new ventures underestimate this cost of acquiring customers. If this cost exceeds the ability to monetize those customers, the business model is not viable. It is even stated that this issue is the second largest cause of start-up failure [58]. Therefore, it is crucial to investigate it in this context. This is often done via an acquisition costs vs. customer lifetime value analysis.

Acquisition costs vs. customer lifetime value analysis Acquisition costs and customer lifetime value are two characteristics that are used in quantifying sales effort and reward. In this section both characteristics are broken down into constituents and estimated.

The **acquisition cost** is the total cost to acquire one customer. In this case, this is mostly sales time, but also includes free testing membranes and some technical time. Taking all these factors in account, a best and worst case calculation (explained in detail in section F.3.1) leads to an acquisition cost of € 12,000 - € 33,000. This value is relatively low because sales efforts can be concentrated on a limited number of OEMs.

The **customer lifetime value** is the value a customer, once acquired, brings to the company. Since OEMs already have an existing customer base, this value is relatively high: one OEM has, according to its size, from five to more than twenty projects per year. Based on worst, base and best case scenarios (explained in detail in section F.3.1) the customer lifetime value ranges from € 21,000 (worst case) to € 480,000 (base case), and to € 3,000,000 (best case).

Based on both calculations, the ratio of acquisition cost vs. customer lifetime value can be determined. The acquisition cost always remains very low because of the small number of OEMs in the market. The customer lifetime value is low in the worst case scenario, leading to a ratio of 0.6-1.5, which would mean a break-even or possibly a small loss. However, in the base and best case scenario, the customer lifetime value increases strongly, leading to ratios of 0.01-0.07. This means that **one successful customer relationship generates enough profits to drive new sales for a long period**. This analysis shows that the proposed market position is very interesting and profitable.

I.4: Expansion opportunities Besides the traditional direct customers (OEMs), there are expansion opportunities for GreenWater. The easiest opportunity is the membrane replacement market: membranes have to be replaced after their lifetime of approximately 1 to 5 years (depending on the membrane type and application) [59, 60]. Often, companies are confronted with higher than expected, recurring replacement costs - so they are open to potential cost savings in this area. The significantly cheaper membranes of GreenWater are very well suited for this market. However, this market requires more extensive marketing and sales because it is more fragmented. A move to this market is most interesting after a few years of experience and growth.

Residential water treatment and NGOs in third-world countries represent two additional markets. These are particularly well suited because they pay more attention to the environmental sustainability of the products, the second selling point of this technology. However, these markets are very fragmented and difficult to reach. A move to these markets is most interesting after considerable growth of the company.

Perspective II: Product feasibility analysis

In this section, the attractiveness and feasibility of the actual product (UF membranes derived from ABS waste) is investigated in three parts. Part II.1 formulates the unique selling proposition (USP) to identify the overall attractiveness of the product towards the direct customer. Part II.2 defines a market strategy, based on the characteristics of the USP, to see how this product can be positioned in the market place. Finally, part II.3 estimates the potential market share of the product to quantify its commercial potential.

II.1: Unique selling proposition The unique selling proposition (USP) is the identification of the product features that drive the customers across the line of indecision to preference, and ultimately to loyalty. Identifying the USP for a product is crucial as basis for the market strategy: unless you can pinpoint what makes your product unique in the market place, you cannot target your sales efforts successfully. [61, 62]

To identify the USP, the following questions should be asked: what problem does GreenWater solve for the OEMs? Why should they consider switching to GreenWater for their membrane supply? Three selling points have been identified:

1. **Financial:** because of a competitive advantage in raw material costs, the membrane price can be chosen at 15% below the cheapest competitor (see further).
2. **Strategic:** many end-users do not install an internal water recycling system because of the high investment cost. Because of the significant decrease in membrane cost, the OEMs can reduce this investment cost and approach a new customer segment: smaller, less financially strong companies (*e.g.* SMEs).
3. **Public relations:** by using plastic waste derived membranes, the OEMs and the end-users can profile themselves as a green company.

II.2: Market strategy The product needs to be well positioned in the market place according to its unique selling characteristics. A possible market strategy is determined on two levels:

1) Market strategy towards customers There are two essential elements in marketing towards customers. The first is the **membrane price**: based on the competitive advantage in raw materials, the price can be set below the cheapest competition. Based on a benchmark analysis (see appendix E, the competitor's prices range between € 70 and € 130 per m^2 membrane area (incl. VAT). It is chosen to set the price 15% below the cheapest competitor, at **€ 60/$\mathbf{m^2}$** (incl. VAT).

Secondly, there is the sustainability characteristic. Here, a major risk presents itself: the quality perception. Plastic waste derived membranes can be perceived as being of lower quality. To counter this perception, a 'no cure, no pay' policy can be used as selling argument. In addition, using the scientific results obtained in this thesis and from a future pilot test can help to gain credibility. Having a positive quality perception is necessary in order to be able to use the sustainability of the product to our advantage.

These are two general elements that can be used during the sales procedure. However, in order to convince the OEM, it is necessary to go more specific. Any OEM typically focuses on one or a few industries (*e.g.* the milk pre-concentration industry). When approaching the OEM, it is crucial to have concrete test results ready for the typical applications in the OEM's target industries. Such concrete evidence of the applicability of the plastic waste derived membranes for the OEM's typical customers, together with the general elements (price and sustainability), can be decisive to convince the OEM to switch to GreenWater for its membrane supply.

2) Market strategy towards competitors The existing competition can act in a number of ways. A typical way is to lower their price, for example by offering discounts to loyal customers. However, because of the significant competitive advantage over the competition for raw material costs, GreenWater is able to cope with such price reductions. The competition can also give the impression that plastic waste derived membranes have a lower quality. It is important to tackle this issue from the beginning, using the mentioned 'no cure, no pay' approach.

Competitors can also respond by trying to copy the product. The intellectual property strategy (see section 6.2.2) is to take an i-DEPOT. This does not prevent other companies from copying, but protects from any of their patent claims and keeps the proprietary information confidential. To copy the product, the competitor must investigate different membrane compositions and gain insight in the different sorts of plastic waste. This takes time: GreenWater is expected to have a first mover advantage in the field of plastic waste derived membranes. In this period without competition for such membranes, specific knowledge and expertise can be built up, which ensures a competitive edge in the future. More specifically, a significant lead is expected on the following elements:

1. Experience with plastic waste sources: as discussed in chapter 5, there are many possible issues to be overcome when dealing with plastic waste. The analysis and (more important) the solutions proposed in this thesis can give a serious competitive advantage during start-up.

2. Experience with plastic waste treatment & production: a head start in membrane production with no competition can give invaluable experience in necessary treatment steps and scalable production methods.
3. Head start with subsidy applications with the governments.
4. Image as innovative player on the market.

II.3: Potential market share To evaluate the commercial potential of the product, it is interesting to investigate the potential market share it can attain. This estimation is based on a PPH analysis, which divides a company's market share into three measurable constituent parts: product coverage (P), sales presence (P) and hit rate (H). By quantifying these individual parts, based on the product characteristics, the sales approach and the market strategy, a reasonable estimate for the market share can be made. In a next stage, this methodology also allows to focus marketing and sales efforts. [63]

Product coverage: 4%. The product coverage is a measure of the degree to which the product offering is considered a viable alternative to the end-user [63]. By dividing the end-user market into its constituents, it is found that the product, UF membranes, covers about 4% of the total membrane industry, and represents a € 700 million industry (see section F.3.2 for the detailed estimation).

Sales presence: 2%. The sales presence is a measure of how often the direct customer considers your offering at the time of making a purchase [63]. First there is a geographical constraint: initially limiting the sales presence to the Belgian market (approximately 4% of the global market) is most logical. Secondly there is the limitations of the sales team: in Belgium itself, it would be overambitious to try targeting all the OEMs from the start. A more modest amount, say 50% of all OEMs, seems more appropriate. Taking all factors together, the sales presence is 2% (see section F.3.2 for the detailed estimation).

Hit rate: 5% - 10%. The hit rate measures how often the sale is won [63]. The membranes of GreenWater represent a significant improvement compared to conventional membranes. However, plastic waste derived membranes may be perceived as being of lower quality. This can be countered with the experimental results, but a successful pilot test may be needed to convince OEMs. Besides, being a new player in the market can bring additional difficulties (*e.g.* existing sales contracts). We estimate a hit rate of 5% initially, rising to 10% if accompanied by successful pilot test results.

The market share can be calculated using the following equation [63]:

$$Market\ share = (product\ coverage \cdot sales\ presence \cdot hit\ rate) \cdot total\ market\ size$$

Based on the total membrane industry of € 20 billion, the preliminary estimate for the **market share is € 600,000, rising to € 1.2 million** if accompanied by successful pilot test results. This analysis shows there is a considerable potential market share and turnover possible for a starting venture. When growing, as the hit rate and sales presence increase gradually and the total industry keeps growing at high rates, a considerable turnover is possible. Section F.3.2 provides all the details of the calculations.

Perspective III: Financial feasibility

This section investigates the overall financial attractiveness of GreenWater. Part III.1 forecasts the sales and costs of GreenWater. Parts III.2 and III.3 develop a three-year income statement and a break-even analysis based on these forecasts to quantify the financial attractiveness. Finally, part III.4 discusses the possible ways for funding the initial investment needed to start up GreenWater.

III.1: Forecasts. This section discusses the forecasts made in the economic model for the sales and costs of GreenWater. These forecasts are essential as they provide the basis for the pro forma financial statements of the next section.

The sales forecasts in the economic model are based on an intuitive, bottom-up approach, by estimating the number of clients and the value of these clients. The approach and the specific assumptions and figures are discussed in detail in section F.2.1.

The first two years are typically slow start-up years: it is conservative not to expect too many sales in this period. The estimated sales are modest in the first year (500 m^2 or € 25,000) and second year (2,000 m^2 or € 100,000). After these two initial years, the start-up difficulties are expected to end. The company should have grown and have built up a solid sales experience. Therefore, in the third year, GreenWater is expected to generate stable revenues (9,500 m^2 or € 470,000).

A good ”gut check” for the turnover of the third year, is to compare it with the results from the PPH analysis executed in the previous section. PPH analysis is a top-down approach based on the potential market share, and led to an annual turnover estimation of € 600,000. This is in the same order of magnitude as the turnover estimated for the third year by the intuitive, bottom-up approach; and therefore gives some confidence to the estimated values. More details on the sales forecasts can be found in section F.2.1.

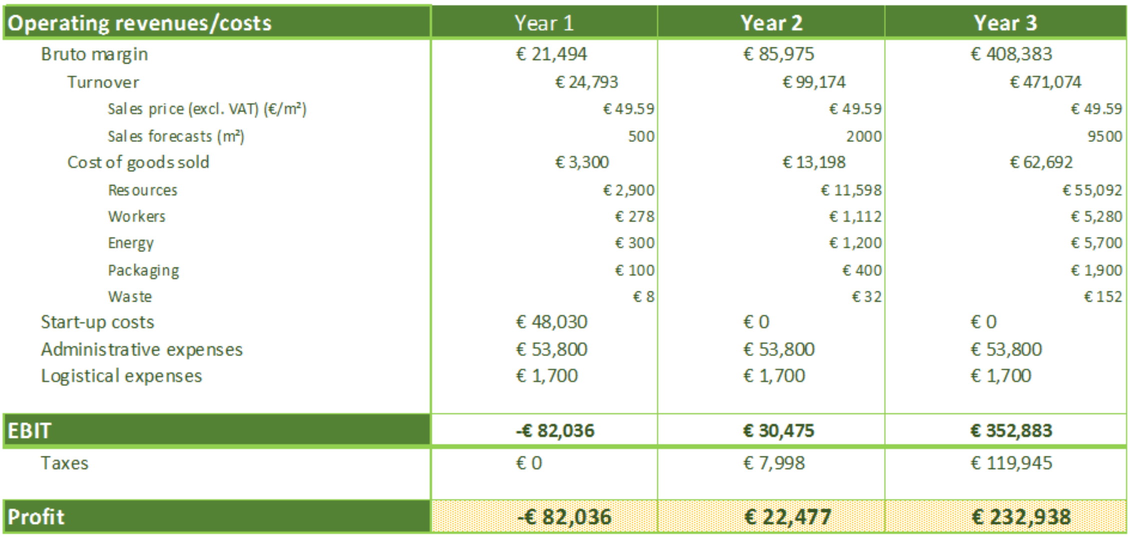
The costs are split in two parts: (i) the variable costs, referred to as the cost of goods sold (COGS) and (ii) the fixed costs, called the general and administrative expenses (GAE). Both costs are estimated in the economic model based on dividing the costs into cost categories and further into specific costs which can be estimated more easily. More details are provided in section F.2.2.

The COGS is estimated at € 7.17/m^2 membrane surface. For this specific case, a price of ABS waste of 30% below virgin ABS is used. However, using waste streams with a low demand (for example EPS waste, which is 98% less expensive than virgin EPS) could provide a more significant cost advantage. It is key to investigate these streams in the future. The GAE are estimated at a one-off investment of € 48,000 and a recurring € 55,500 annual fixed costs.

III.2: Pro forma income statement. In this section, financial projections are made for future periods. Figure 6.3 shows a three-year income statement, developed based on the economic model. The income statement takes into account the expected revenues and expenses and shows whether GreenWater makes a profit or might experience a loss.

In the first year, expected sales are low, leading to low revenues. The initial investment and yearly fixed costs lead to a significant loss of about € 80,000. In the second year however, the revenues are enough to cover all the costs, leading to a small profit of about € 20,000.

Finally, in the third year, the actual potential of GreenWater is shown. Sales of 9,500 m^2 membranes are enough to generate a **profit of about € 230,000**. This is mainly due to the **low variable costs**, which is a direct consequence of using inexpensive resources and represents the competitive advantage of GreenWater.



Operating revenues/costs	Year 1	Year 2	Year 3
Bruto margin	€ 21,494	€ 85,975	€ 408,383
Turnover	€ 24,793	€ 99,174	€ 471,074
Sales price (excl. VAT) (€/m²)	€ 49.59	€ 49.59	€ 49.59
Sales forecasts (m²)	500	2000	9500
Cost of goods sold	€ 3,300	€ 13,198	€ 62,692
Resources	€ 2,900	€ 11,598	€ 55,092
Workers	€ 278	€ 1,112	€ 5,280
Energy	€ 300	€ 1,200	€ 5,700
Packaging	€ 100	€ 400	€ 1,900
Waste	€ 8	€ 32	€ 152
Start-up costs	€ 48,030	€ 0	€ 0
Administrative expenses	€ 53,800	€ 53,800	€ 53,800
Logistical expenses	€ 1,700	€ 1,700	€ 1,700
EBIT	**-€ 82,036**	**€ 30,475**	**€ 352,883**
Taxes	€ 0	€ 7,998	€ 119,945
Profit	**-€ 82,036**	**€ 22,477**	**€ 232,938**

Figure 6.3: Three-year income statement

III.3: Break-even analysis. Break-even analysis is a more tangible tool to evaluate the financial attractiveness of the proposed business model. It quantifies the amount of units that need to be sold in order to "break even", *i.e.* generate exactly enough revenues to cover all the costs. This allows to evaluate the sensitivity of the business model to the amount of membranes sold.

The break-even analysis depicted in figure 6.4 shows that, to cover the fixed and variable costs, a sales volume of 1300 m^2 (€ 65,000) is sufficient. **This shows the potential of the business model of GreenWater: the low variable costs make it very profitable, even if (initially) not many sales are made.**

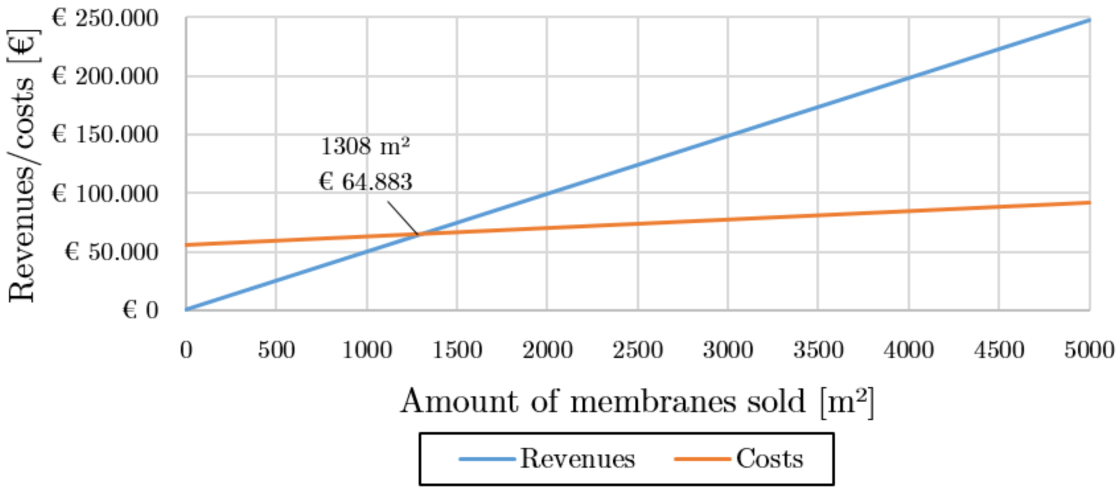


Figure 6.4: Break-even analysis

III.4: Funding. To start GreenWater, a certain amount of funding is required, for two main purposes [56]:

1. Capital investments: purchasing equipment, buying property, *etc.* This investment is estimated at € 48,000 (details can be found in section F.2.2).
2. Cash flow challenges: the delay in time between spending to generate revenues and earning income from this spending, can cause a company to run out of money. This is one of the primary reasons new ventures fail [56]. The spending includes fixed and variable costs that must be paid up front. In the most pessimistic scenario, all the fixed and variable costs shown in the income statement are made, but no revenues follow them during the first three years. This conservative scenario would lead to an additional necessary funding of € 246,000.

Based on these two estimates, a total funding of approximately € 295,000 is required. It is risky to place too much reliance on one source of funding. Therefore, it is crucial to have a good understanding of the different types of funding that are available to generate this amount. Four major types of funding are typically identified [56]:

1. Personal financing: personal funds, sweat equity (the value of the time & effort invested by the entrepreneur) and investments by friends & family.
2. Equity funding: exchanging a partial ownership for funding. The most interesting type is via business angels, which are individuals (*e.g.* professors or retired entrepreneurs) that invest typically € 10,000 - € 500,000. This is attractive, since they are incentivized investors that introduce valuable expertise and business experience.
3. Debt financing: **rewards-based crowdfunding** represents an attractive alternative. The idea is that individuals make relatively small contributions in return for some (future) product or amenity. GreenWater represents an attractive poster project that might convince many individuals. A well-known precedent is the crowdfunding campaign of ”Ocean Cleanup” which raised over € 2 million [64].
4. Other sources: leasing instead of purchasing, applying for governmental/private grants (*e.g.* IWT[2]), and establishing strategic partnerships are also interesting sources of funding.

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[2] IWT, the Flemish government agency for Innovation by Science and Technology, provides grants (€ 17,500 - € 250,000) for new SMEs that contribute to technological innovation [65].

6.3 Conclusion

This chapter evaluates the overall competitiveness of the most successful membranes. Based on the experimental membrane performance results of chapter 5, the membranes are linked to specific applications. The PS-A and PS-B membranes show potential for application in (i) less demanding NF applications (*e.g.* in a hybrid set-up) and (ii) as support layer for thin-film composite membranes.

The ABS-A and ABS-B membranes are tested for MF and UF. The membranes have a too low permeability to be applied in MF, but have the right characteristics for UF. Especially the ABS-B membranes, which have a very high permeability combined with an excellent retention, show **much potential for UF** applications.

Inspired by the concept of academic entrepreneurship, the second section of this chapter proposes - and applies - a new approach to (i) estimate the business potential of a new technology and (ii) set the ground for the development of a spin-off to commercialize it. The approach consists of two steps:

1. Develop a business model around the new technology from a spin-off perspective.
2. Analyze the feasibility of this business model, by looking more closely at:
    a. Industry & market feasibility
    b. Product feasibility
    c. Financial feasibility

The **business model** for this technology is aimed at industrial water treatment as end-users. However, it is shaped around OEMs as direct customers. Partnerships with either module producers or OEMs are found vital by gaining an existing customer base and introducing market experience and expertise.

The **industry and market** seem feasible. The emerging membrane industry, having high growth figures and little competition, is very attractive. However, the general W&WWT market is more difficult to enter which may cause augmented start-up issues. The market position, based on OEMs as direct customers, is calculated to be very profitable, because OEMs provide an existing customer base and their market is highly consolidated.

The **product** has three key selling points to convince OEMs, based on the low cost and high sustainability of the plastic waste raw materials. The potential market share that can be attained in an early stage is estimated at € 600,000 - € 1,200,000, which is considerable for a starting venture.

Financially, GreenWater is expected to have a profit of € 230,000 in the third year. This is mainly due to the low variable costs, which is a direct consequence of using inexpensive resources and represents the competitive advantage of GreenWater. The risk is also small, since even a limited amount of annual sales (1300 m^2) is enough to break even. To start up, funding of approximately € 300,000 is required. Addressing business angels and implementing a crowdfunding campaign are attractive types of funding for GreenWater.

Chapter 7

General conclusions and future outlook

7.1 General conclusions

Water scarcity and plastic waste are two well-known, global problems. For **water scarcity**, treatment and reuse of wastewater is the most promising option to decrease water consumption [13]. New technologies are needed to achieve this in a cost-efficient way. For **plastic waste**, an increase in recycling is necessary, for both economic and ecological reasons. This requires a perception change towards recycled plastics.

For treatment and reuse of wastewater, membrane technology is found to be an attractive alternative because of shifting policy and the need to reduce energy use and costs. However, the overall success of membrane technology is lagging behind the expectations formulated from the technology's inception [25]: today, membrane technology is not applied to its full potential in industry.

This thesis research aims to develop a new generation of cheaper, green membranes, by **studying the use of a new source for membrane materials: plastic waste**. This research can lead to a cost-effective and more environmentally sustainable membrane technology. Both factors are essential in incentivizing industry to implement membrane technology.

To achieve this goal, the approach used in this research is based on three consecutive phases:

1. Study the fundamental potential of plastic waste derived membranes on lab-scale.
2. Investigate the scaling up of the membranes from lab-scale to industrial scale.
3. Evaluate the industrial applicability of the technology.

7.1.1 Phase I: Fundamental study

"Can membranes be made from plastic waste?"

The answer is *yes*: three types of post-consumer plastic waste (PS, EPS, and ABS) lead to the production of high-quality membranes.

Experimental analysis with an aqueous dye solution shows that the retention of plastic waste derived membranes is in the range of a selection of commercial NF membranes or slightly below. Their permeability is, on average, better than that of the selection of commercial NF membranes.

Plastic waste derived membranes are fundamentally possible and promising compared to commercial NF membranes.

7.1.2 Phase II: Scaling up

"Is the technology scalable?"

The answer is *maybe*: the negative technical and commercial consequences of using plastic waste as a raw material for membrane production can be resolved. Nevertheless, important legal issues remain.

Based on expert interviews and lab experiments, it is found that using plastic waste instead of virgin plastics to produce membranes has nine effects - of which seven are negative.

An important technical problem is the inconsistency of post-consumer waste, leading to a variable membrane quality. The proposed solution is the use of more consistent post-industrial waste. Fourteen large-scale post-industrial waste streams are investigated for membrane production, and four of them (two PS and two ABS waste streams) are found to have potential for commercial membrane filtration.

However, one consequence on the legal level remains unresolved. It relates to the additional regulations concerning the use of plastic waste in membranes. Though it does not seem to be impossible to resolve, this legal issue can burden the application of this technology, and should be further investigated.

The technology seems technically and commercially scalable when switching to post-industrial plastic waste, but the legal aspect needs further investigation.

7.1.3 Phase III: Application

"Is the technology competitive for industrial applications?"

The answer is *potentially yes*: based on indicative experiments, the membranes seem technically fit for industrial application. An economic analysis shows they are also competitive.

First, the membranes are evaluated technically for different applications. Experimental analysis with an aqueous dye solution shows that PS-waste derived membranes are slightly below commercial NF quality. This means they may be applied in (i) less demanding NF applications (*e.g.* in a hybrid set-up) and (ii) as support layer for thin-film composite membranes.

Experimental analysis with an aqueous beads solution shows that ABS-waste derived membranes have an excellent retention and the required permeability for high-quality commercial UF.

Secondly, the membranes are evaluated in a business context, based on a new two-step approach:

1. Develop a business model around the new technology from a spin-off perspective.
2. Analyze the feasibility of this business model.

The business model for this technology is aimed at a university spin-off for industrial water treatment. It is shaped around OEMs as direct customers. The feasibility of this business model is evaluated from three perspectives:

1. Industry & market feasibility: the emerging membrane industry, having high growth rates and little competition, is very attractive. However, the general W&WWT market is more difficult to enter which may cause augmented start-up issues. The market position, based on OEMs as direct customers, is calculated to be very profitable, because OEMs provide an existing customer base and their market is highly consolidated.

2. Product feasibility: plastic waste derived membranes have three key selling points to convince OEMs, based on the low cost and high sustainability of the plastic waste raw materials.

3. Financial feasibility: the spin-off is expected to have a profit of € 230,000 in the third year. This is mainly due to the low variable costs, which is a direct consequence of using inexpensive resources and represents the competitive advantage. The risk is also small, since even a limited amount of annual sales (1300 m^2) is enough to break even. To start up, funding of approximately € 300,000 is required.

Membranes derived from post-industrial PS and ABS waste have potential for industrial application and a spin-off to commercialize them is feasible.

7.2 Future outlook

This thesis research is only the initial stage of an ambitious, more encompassing project. The goal of this project is to **fully develop plastic waste derived membranes commercially based on a university spin-off**. Ultimately, this allows to bring the technology to the industry and into widespread application. This is essential to achieve real progress in solving global problems of water scarcity and plastic waste. However, more work and research is necessary to reach these goals:

First, more **experimental analysis** is necessary to confirm the applicability of the membranes in industrial applications. This thesis research investigated one type of solute for NF and one type for UF: this scope should be broadened to various types of solutes and concentrations. To identify important operational characteristics of the membranes, more long-term testing of real industrial water streams is also required. This allows to identify fouling behavior, ease of cleaning, and long-term membrane stability in industrial environments. To gain specific knowledge in this area, a stay at the Institute for Membrane Technology (ITM-CNR) in Cosenza, Italy, can be considered.

Secondly, **membrane module design** is necessary to transform the membrane sheet to an actual product that can be used in industry. Today, practical knowledge of membrane modules represents a gap in expertise in the research group at KU Leuven. Further research, combined with industry partnerships, can allow for a better understanding of the fundamental and practical implications of module design.

Thirdly, **industrial membrane production** on a large scale must be investigated. Industrial production, and the implications this has on raw material choices and membrane performance, is crucial in commercializing this technology. Another element of importance in industrial membrane production is a generalization of the desired waste stream characteristics. The initial work of this thesis in this area should be continued. Ideally, this leads to easy selection of potential waste streams based on testing a few material characteristics.

Finally, the **business opportunities** identified in the economic analysis should be further pursued. This thesis is based on high-value plastic waste streams, with a corresponding high price. However, some low-value plastic waste streams (mixed streams, EPS waste streams, 3D printing polyamide waste streams, *etc.*) are identified and can represent a significant competitive advantage and an increased societal impact. Therefore, it is crucial to stay open for such opportunities where low-cost waste streams can be valorized in membrane production, and investigate them further. Apart from this, it is also necessary to investigate the legal issues concerning the application of plastic waste derived membranes.

Appendices

Appendix A

UV-visible spectrophotometry standard curves

To evaluate the membrane performance, retention tests are conducted with feed solutions containing compounds that can be detected by UV-visible spectrophotometry. UV-visible spectrophotometry refers to absorption spectroscopy in the ultraviolet-visible spectral region. In this case, only the visible spectral region is used. The absorption in the visible region is related to the color of the solution. [66]

The measured absorption can be related to the concentration of the solutes involved. Over a certain concentration range, this relation is linear and described by the Beer-Lambert law:

$$A = \log_{10} \frac{I_0}{I} = \epsilon c L$$

Where A is the measured absorbance, I_0 the intensity of the incident light at a given wavelength, I the transmitted intensity, ϵ the extinction coefficient or molar absorptivity, c the concentration of the absorbing species, and L the path length of the sample. [66]

The wavelengths of maximum absorption are determined for all compounds based on determining a full absorption spectrum. These wavelengths are 618 nm (malachite green oxalate), 498 nm (congo red), 427 nm (MF beads), and 428 nm (UF beads).

Standard curves are prepared for all the used solutes, in order to check the linearity of the used concentration range and therefore the applicability of the Beer-Lambert law. In case of linearity, the retention of the compounds can be determined via the linear relation between absorbance and concentration, using the following equation:

$$R = \left(1 - \frac{C_p}{C_f}\right) \cdot 100\% = \left(1 - \frac{A_p}{A_f}\right) \cdot 100\%$$

Where R is the retention (%), C_p the permeate concentration, C_f the feed concentration, A_p the absorbance of the permeate, and A_f the absorbance of the feed.

Figure A.1 shows that for malachite green oxalate and congo red, the relation between absorbance (at the wavelength of maximum absorption) and concentration is linear (R^2 is sufficiently close to 1) over the concentration range 0.014 ppm –14 ppm (corresponding to

99.9% - 0% retention).

Figure A.2 and figure A.3 show that for the MF beads and UF beads, the relation between absorbance and concentration is also linear (R^2 is sufficiently close to 1) over the concentration range 0.2 ppm –100 ppm (99.8% - 0% retention) and 2.5 ppm - 500 ppm (99.5% - 0% retention) respectively.

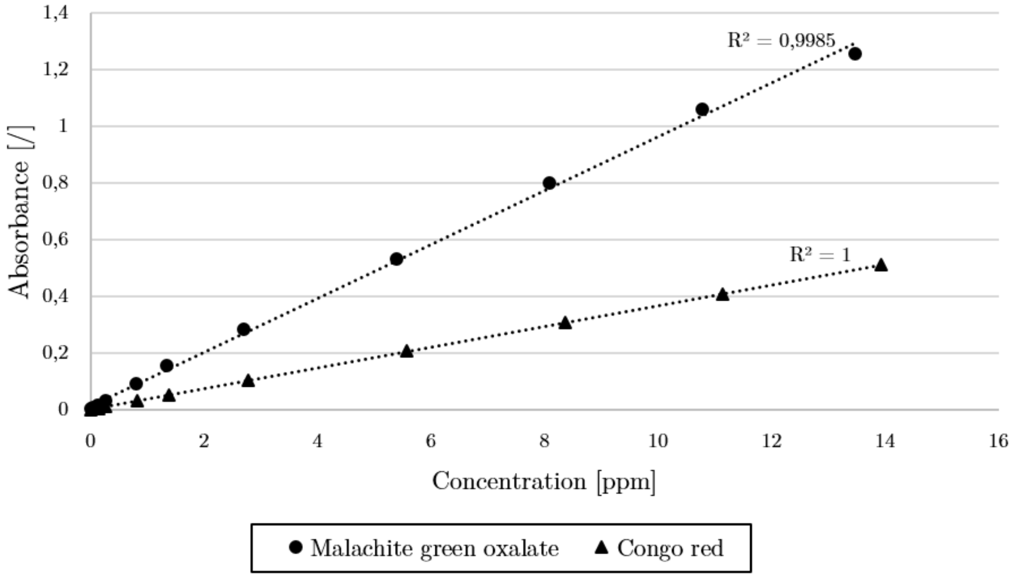

Figure A.1: Standard curve for aqueous dye solutions

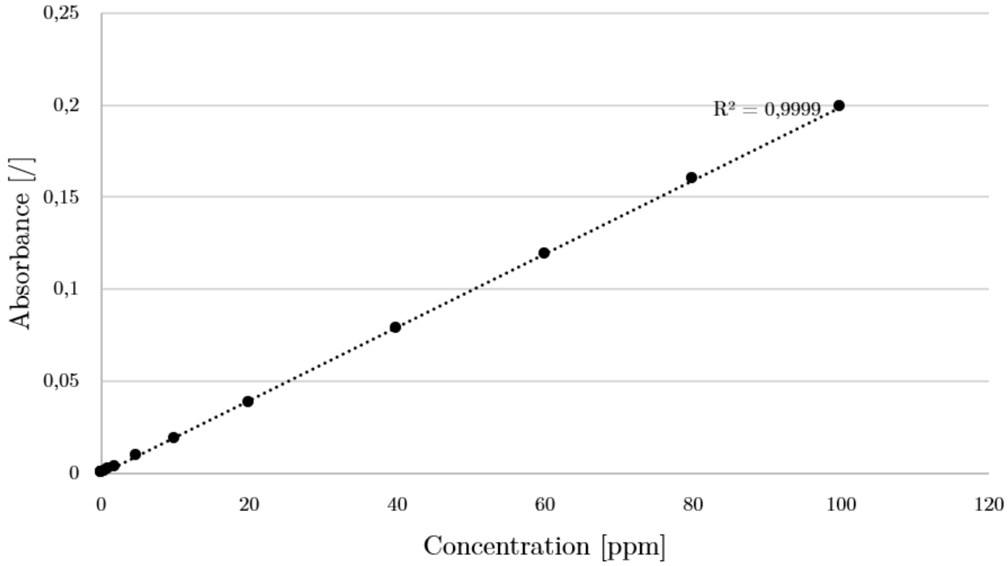

Figure A.2: Standard curve for MF beads

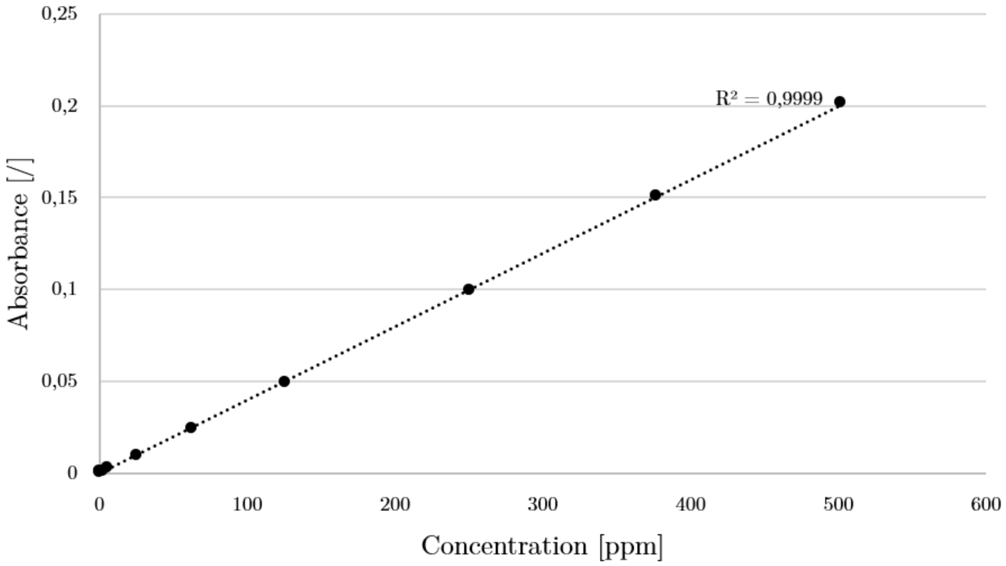

Figure A.3: Standard curve for UF beads

Appendix B

Practical measures for defect-free membrane production

The immersion-precipitation procedure, as described in literature [5], does not necessarily produce good quality, defect-free membranes. This is because some production parameters are not mentioned or not explicitly specified. Based on a troubleshooting approach, the following six practical measures or actions – in addition to the existing procedure – are found to be essential in manufacturing good quality membranes:

1. Support layer attachment: in attaching the support layer to the glass casting plate, it is crucial to attach it very tightly. It should be visually inspected that no air bubbles are present between the support and glass.
2. Wetting of support layer: the wetting of the support layer should be done by spraying solvent with a syringe, from the center of the support layer toward the sides, to prevent the trapping of air bubbles under the support. It should be visually inspected that no air bubbles are present.
3. Coagulation time: various coagulation times are reported in literature, ranging from 15 minutes to 24 hours. This should be investigated for each specific membrane type. In the case of this thesis research, 60 minutes proved to be sufficient.
4. Membrane curling (non-solvent bath): to prevent the membrane from curling up in the non-solvent bath, weights can be placed on the four corners of the membrane.
5. Membrane curling (conservation): to prevent the membrane from curling up in the conservation containers, they can be pressed upon lightly with a weight, or they can be conserved in a tray using weights to keep it down (*cf.* the non-solvent bath).
6. Casting thickness: a casting thickness of 100 µm is shown to be prone to defects. A thickness of 200 µm - 250 µm is sufficient. [5,45]

Appendix C

Raw material analysis

An analysis of the properties of the raw materials is performed to be able to generalize the discussion of waste stream characteristics that are important for membrane manufacturing. Ideally, a waste stream could be evaluated for membrane manufacturing based on testing a few parameters, allowing an easy selection of potential waste streams.

As stated in section 5.2, the investigated properties are limited to (i) the chemical composition of the polymer material (determined by DSC analysis) and (ii) the viscosity of the polymer material (determined by rheology). More detailed information on both analyses is provided in this appendix.

C.1 DSC analysis

The differential scanning calorimetry (DSC) analysis is performed using a DSC Q 2000 (TA Instruments). DSC analysis allows to determine a number of thermal properties of a sample (glass transition temperature, melting temperature, *etc.*). These thermal properties can be seen as a ”fingerprint” of a certain material. Moreover, considering the origin of the samples, it can be assumed that they are all commodity polymers, limiting the amount of possibilities. Therefore, in this case, the polymer type of a sample can be determined with good certainty using DSC. [47,48]

This section provides technical details of the analysis and the conclusions. The section is organized in three parts of similar samples: (i) post-industrial PS samples, (ii) post-consumer PS samples, and (iii) ABS samples.

C.1.1 Post-industrial plastic waste: PS samples

Based on the DSC analysis of the post-industrial PS samples (see figure C.1), it can be concluded that samples IND-PS-A, IND-PS-B and IND-PS-FR are most likely polystyrene. However, the sample IND-PS-C is more similar to polycarbonate, while the sample IND-PS-D is probably a blend of polystyrene and a crystalline polymer, like polyethylene. The technical reasoning behind this conclusion is given here:

IND-PS-A A glass transition temperature is identified at 90°C - 100°C, which is characteristic for polystyrene.

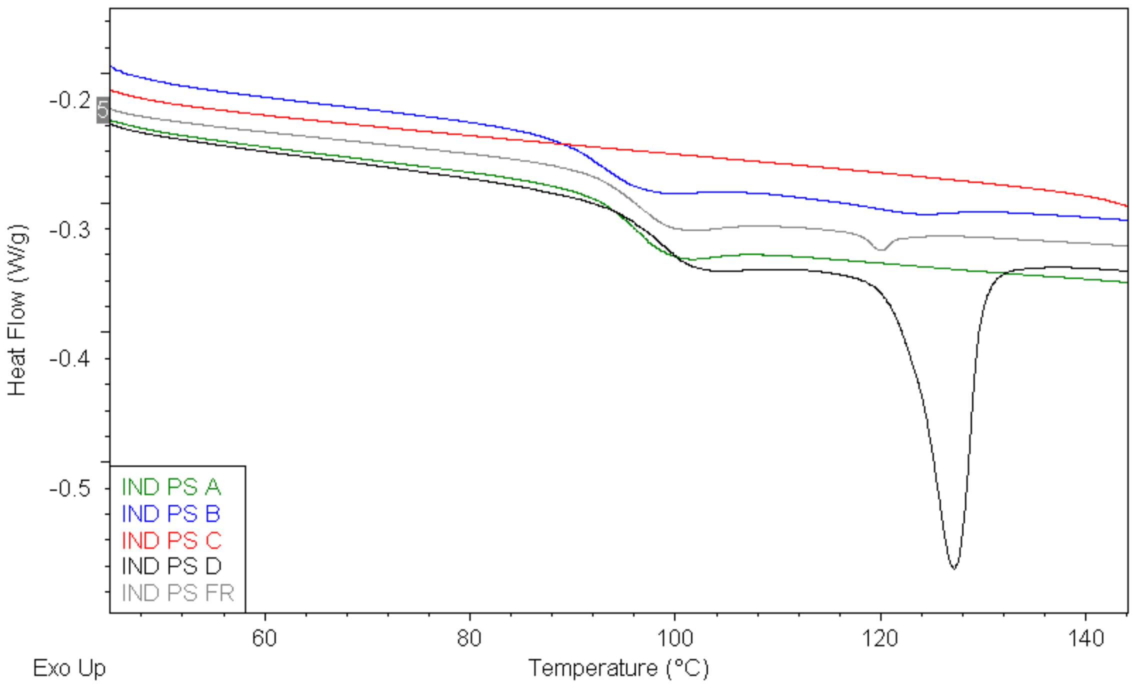

Figure C.1: DSC analysis of post-industrial PS samples

IND-PS-B A glass transition temperature is identified at 90°C - 100°C, which is characteristic for polystyrene. Potentially, another thermal phenomenon can be identified at 120°C - 130°C, which could mean there is an impurity or blend of polymers.

IND-PS-C No glass transition temperature can be identified at 90°C - 100°C. A glass transition temperature can be identified at 140°C - 155°C, which could mean it is a polycarbonate or some special form of polystyrene (see figure C.2 to see similarity with a polycarbonate grade).

IND-PS-D A glass transition temperature is identified at 90°C - 100°C which is characteristic for polystyrene. A melting temperature is identified at 120°C - 130°C, which could mean this sample is a blend between polystyrene and a semi-crystalline polymer such as (high density) polyethylene.

IND-PS-FR A glass transition temperature is identified at 90°C - 100°C which is characteristic for polystyrene. The excitation at 120°C is not corresponding to a melting temperature, since it does not return in further heating and cooling cycles. It probably originates from an impurity.

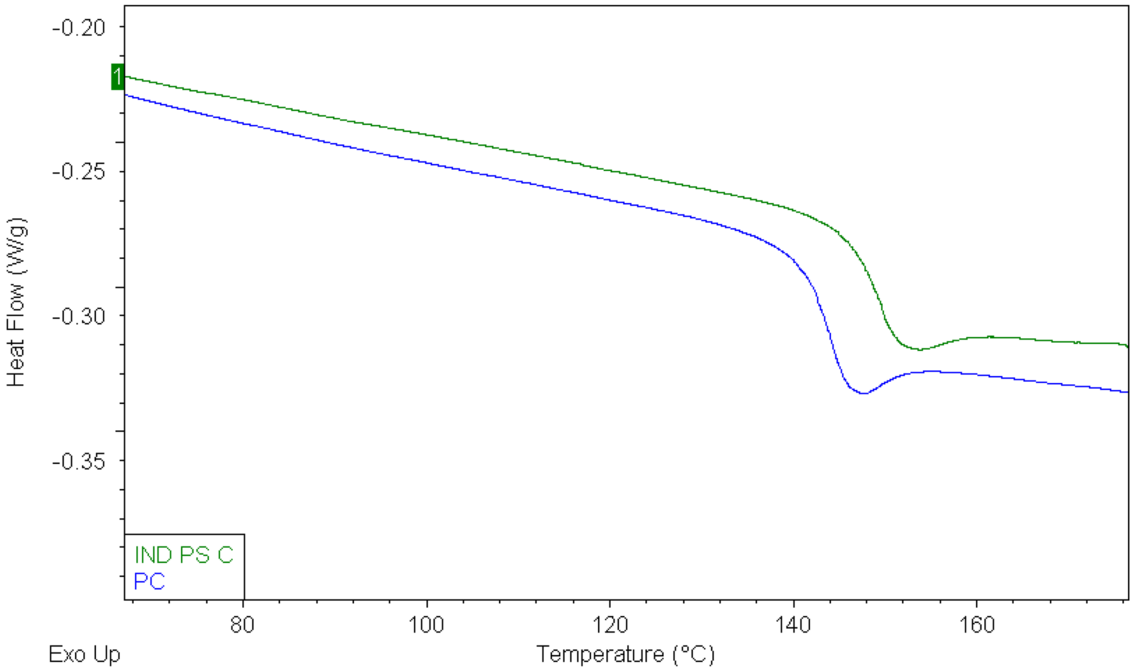

Figure C.2: DSC analysis of PS-C sample and a PC sample

C.1.2 Post-consumer plastic waste: PS samples

Based on the DSC analysis of the post-consumer plastic waste (see figure C.3), it can be concluded that samples SELF-CD-1, SELF-CD-3 and SELF-Plates are PS type polymers. For the SELF-CD-2 sample, this is not certain. It could be a modified PS grade, or even a type of PVC. The technical reasoning behind these conclusions is:

SELF-CD1 (opaque part of first CD case) A glass transition temperature is identified at 90°C - 100°C which is characteristic for polystyrene.

SELF-CD2 (opaque part of second CD case) A glass transition temperature is identified at 80°C - 90°C. A melting-like phenomenon is identified at 120°C. These two observations could indicate a modified PS grade, for example with significant amount of plasticizer (leading to a decreased glass transition temperature), or could indicate a type of PVC (corresponding to the lower glass transition temperature and the presence of a melting point).

SELF-CD3 (transparent part of third CD case) A glass transition temperature is identified at 95°C - 105°C which is characteristic for polystyrene.

SELF-Plates (disposable plates) A glass transition temperature is identified at 90°C - 100°C which is characteristic for polystyrene.

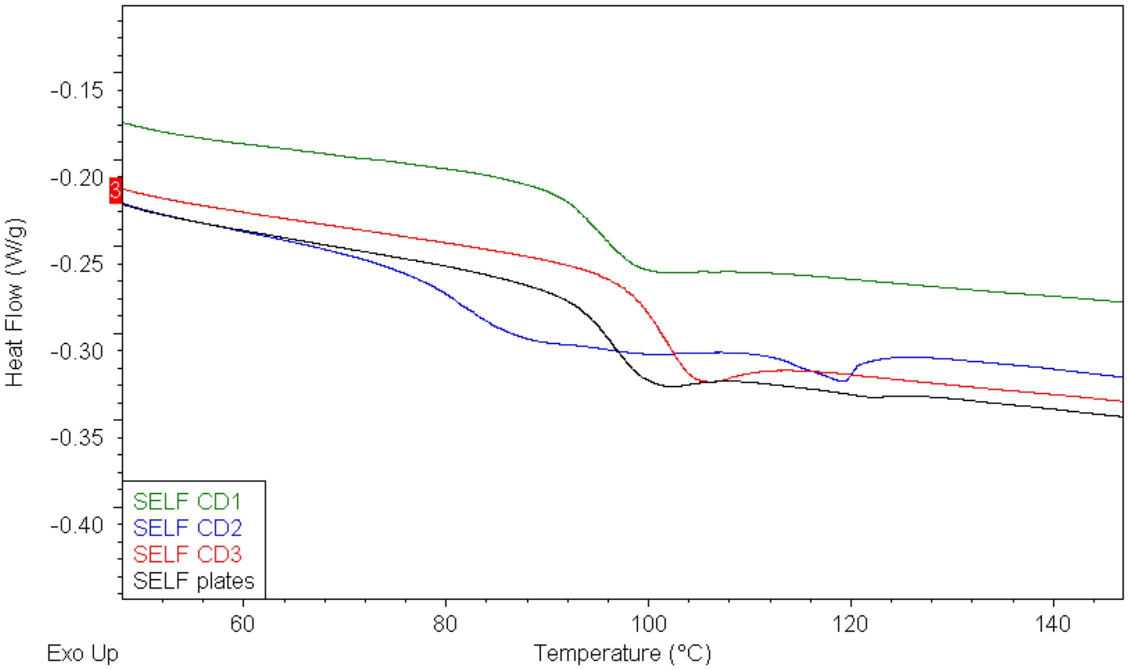

FIGURE C.3: DSC analysis of post-consumer PS samples

C.1.3 Post-industrial & post-consumer plastic waste: ABS samples

Based on the DSC analysis of post-industrial ABS samples (see figure C.4), it can be concluded that both samples (IND-ABS-A and IND-ABS-B) are ABS type polymers, though the foil present on IND-ABS-B is not. Also the collected LEGO® is an ABS type polymer. The technical reasoning is:

IND-ABS-A A glass transition temperature is identified at 110°C which is characteristic for ABS.

IND-ABS-B A glass transition temperature is identified at 110°C which is characteristic for ABS. This sample seems to have a lower heat capacity than IND-ABS-A . This could indicate the presence of inorganic fillers, a film, *etc.*[1] The foil, present on the sample, clearly does not correspond to ABS so it is another polymer (it could be a blend of two semi-crystalline polymers, like polyethylene).

SELF-ABS-LEGO® A glass transition temperature is identified at 100°C. This is a little less than for regular ABS, but can be due to the specific composition of LEGO®.

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[1] The absolute value of the heat flow (vertical axis) is lower for IND-ABS-B than for IND-ABS-A and SELF-ABS-LEGO®. This behavior typically originates from inorganic fillers, because they contribute more to the mass of the sample than to the heat capacity of the sample. The heat flow is normalized by dividing it by the sample mass.

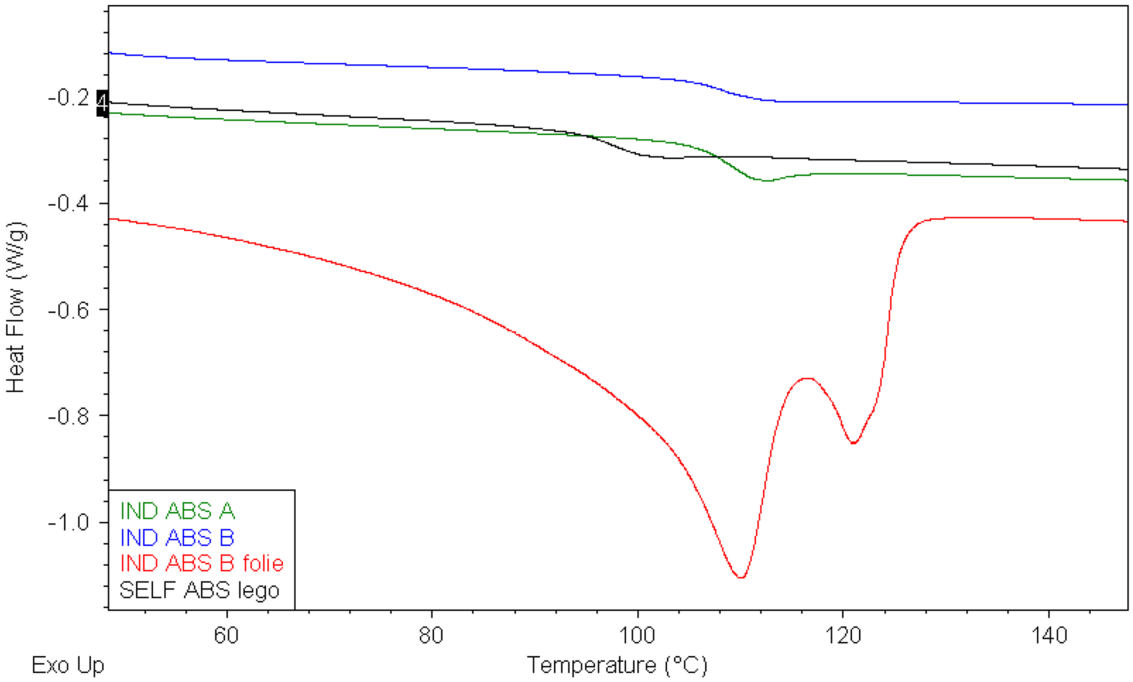


Figure C.4: DSC analysis of ABS samples

C.2 Rheometry analysis

A rheometry analysis has been performed for five post-industrial plastic waste samples (PS-A, PS-B, PS-FR, ABS-A and ABS-B) using an AR 2000ex rheometer (TA Instruments). Strain-controlled tests are performed, by consecutively conducting a peak hold step to check time stability; a strain sweep step to determine the linear viscoelastic regime, in which then a frequency sweep is conducted; and finally a shear rate sweep is conducted to complete the analysis. The latter two are the most important for our study, as they give the viscosity as a function of deformation speed. As can be seen from figure C.5 and figure C.6, these polymers are shear-thinning, with decreasing viscosities at increasing shear rates. Moreover, for polymers, the Cox-Menz rule should be valid, meaning that the shear rate sweeps and frequency sweeps should overlay. This seems to be the case here, confirming the validity of the measurements. [67, 68]

The analysis is conducted at a constant temperature, which is taken at 100°C above the glass transition temperature of the polymer type. For the PS samples, 200°C is used; for the ABS samples, 210°C is used.

The results of the steady state flow step are shown in figure C.5 for each sample. In this case, we are interested in the viscosity at low shear rate (which is closest to the actual situation during phase separation). At low shear rates, it can be seen that the viscosity of all samples moves toward a constant value (Newtonian plateau) [68]. Figure C.5 shows that both ABS samples have a similar viscosity. On the other hand, the three PS samples have a different viscosity. The PS-A sample has the highest viscosity, followed by PS-FR and finally PS-B which has the lowest viscosity. Figure C.6 shows the results of the frequency step. This graph confirms the results of figure C.5, though here the viscosities of samples

ABS-A and ABS-B are even more similar.

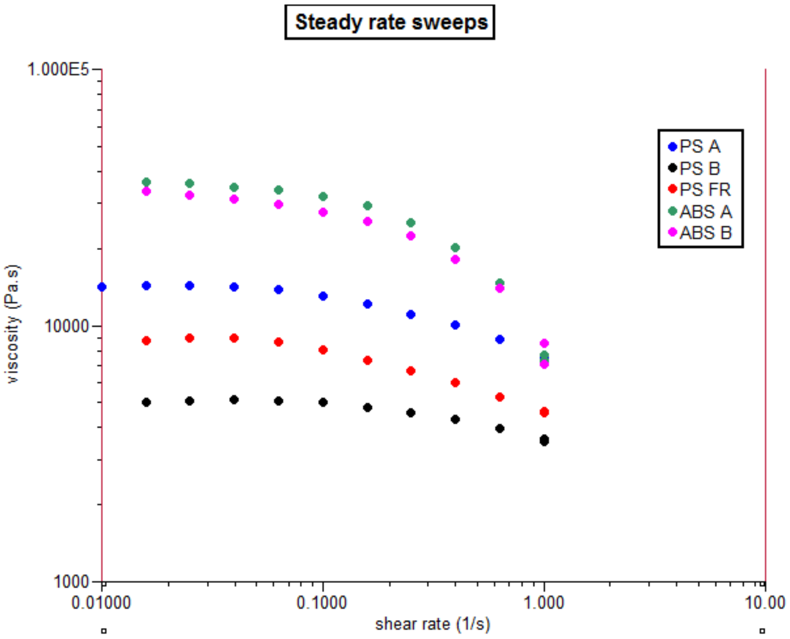


Figure C.5: Rheometry analysis: steady rate sweeps (200°C for PS samples, 210°C for ABS samples)

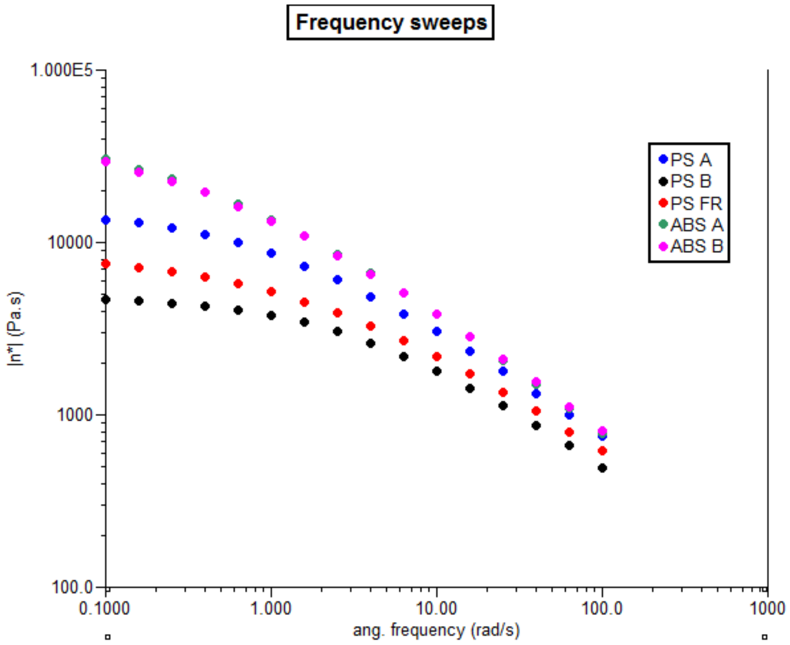


Figure C.6: Rheometry analysis: frequency sweeps (200°C for PS samples, 210°C for ABS samples)

Remark: choice for rheometry A remark must be made on the choice for rheometry experiments in the research context. In the ideal case, viscometry experiments are used to determine the viscosity of the polymer in solution. This mimics the real situation, as the polymer is dissolved (initially) during the phase inversion process. However, in this specific research context, rheometry measurements were more easily available than viscometry measurements, because of safety reasons: using a hazardous solvent in viscometry requires following certain safety procedures. Rheometry experiments are used to determine the viscosity of a polymer in molten state. This is however still related to the viscosity of a polymer solution – it is possible to relate both qualitatively: a high viscosity of a specific polymer type in molten state, is typically associated with a high molecular weight, which in turn is typically associated with a high viscosity of the specific polymer in solution [49].

In this viscosity experiment, we are only interested in relative differences of viscosity to check the hypothesis. Therefore, rheometry suffices and because of its easier availability was also the better choice. If a deeper, more quantitative analysis must be made, then viscometry may be better suited.

Appendix D

Scanning electron microscopy

The cross sections of the PS-A, PS-B, PS-FR, ABS-A and ABS-B membranes are observed by SEM (scanning electron microscopy). Images are made on multiple locations along the membrane cross section. Two images per membrane are selected and shown in this appendix. The first image gives an indication of the sublayer structure, the second image is a magnification to be able to visualize the top layer. The interpretation of the SEM images is based on literature. [22, 45, 46]

IND-PS-A Figure D.1 and figure D.2 show the images for the cross section of PS-A membranes. Figure D.1 shows a typical finger-like membrane structure, with the finger structures having relatively little pores inside of them. Relatively few macrovoids can be identified. This explains a lower permeability. Figure D.2 gives an indication of the top layer thickness (1.86 µm). This is quite large, explaining a high retention.

IND-PS-B Figure D.3 and figure D.4 show the images for the cross section of PS-B membranes. Figure D.3 also shows a finger-like membrane structure. However, there are already more pores inside these finger structures. This explains the higher permeability. Again, relatively few macrovoids can be identified. The top layer thickness is difficult to identify, though figure D.4 seems to indicate it is larger than 1 µm, but smaller than for the PS-A membranes.

IND-PS-FR Figure D.5 and figure D.6 show the images for the cross section of PS-FR membranes. Figure D.5 also shows a finger-like membrane structure. Already some more macrovoids can be identified. Figure D.6 shows these finger structures are more perforated than for PS-A and PS-B. This explains the higher permeability. Figure D.6 indicates a top layer thickness of 466 nm - 841 nm. This can explain the lower retention for PS-FR membranes.

IND-ABS-A Figure D.7 and figure D.8 show the images for the cross section of ABS-A membranes. Figure D.7 shows a finger-like membrane structure, but with many perforations inside the finger structures. There are also many macrovoids. This explains the higher permeability. Figure D.8 indicates a top layer thickness of approximately 168 nm. This very thin top layer can explain the lower selectivity (retention) compared to PS-A and PS-B membranes.

IND-ABS-B Figure D.9 and figure D.10 show the images for the cross section of ABS-B membranes. Figure D.9 shows a finger-like membrane structure, but with many perforations inside the finger structures. There are also many macrovoids. This explains the higher permeability. Figure D.10 is too unclear to indicate the top layer thickness.

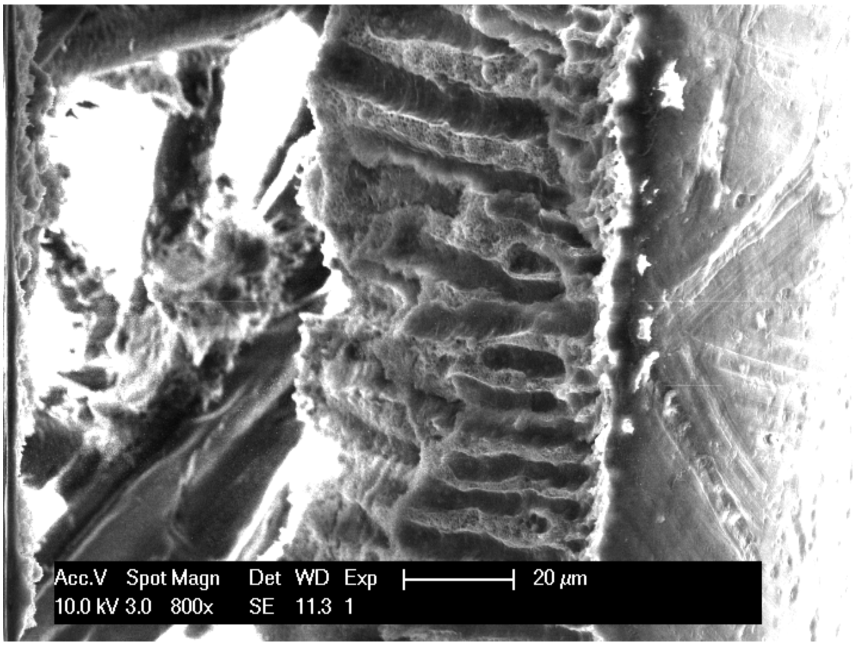


Figure D.1: SEM image of an IND-PS-A sample (magnification 800x)

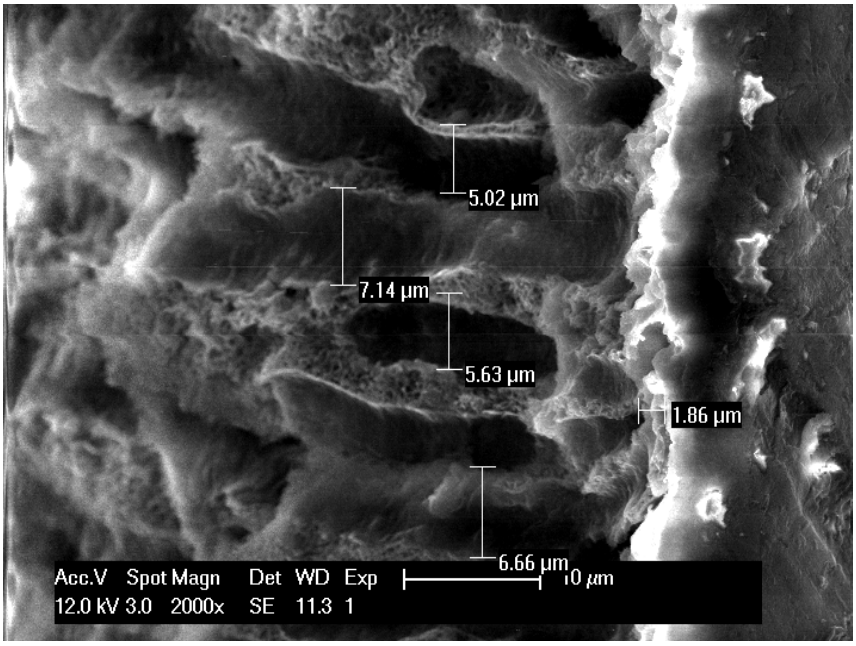


Figure D.2: SEM image of an IND-PS-A sample (magnification 2000x)

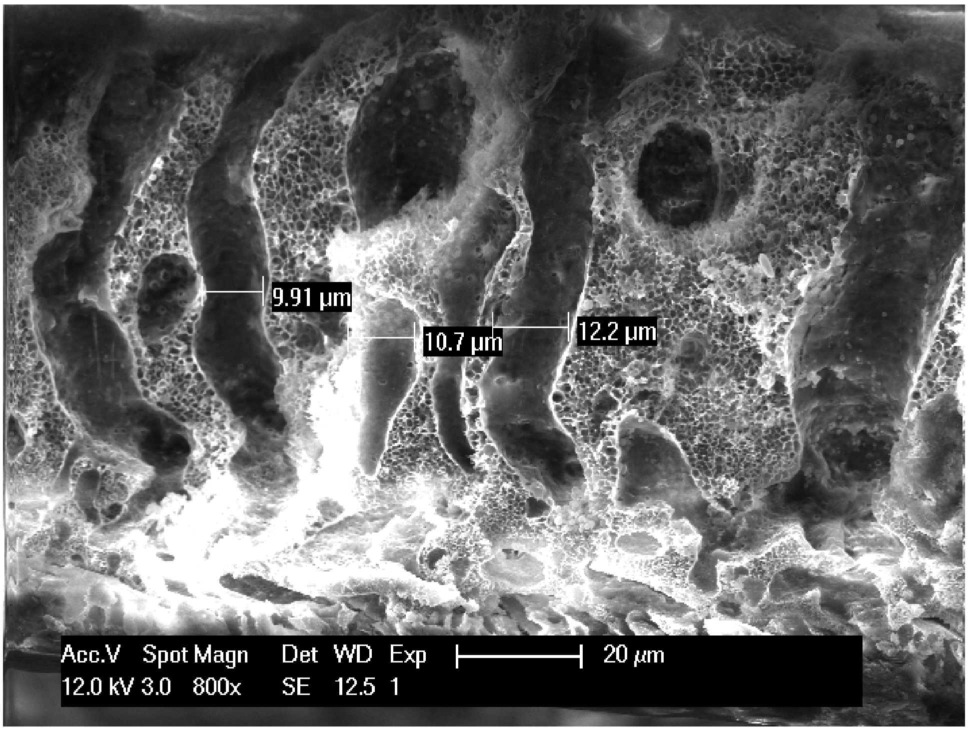


Figure D.3: SEM image of an IND-PS-B sample (magnification 800x)

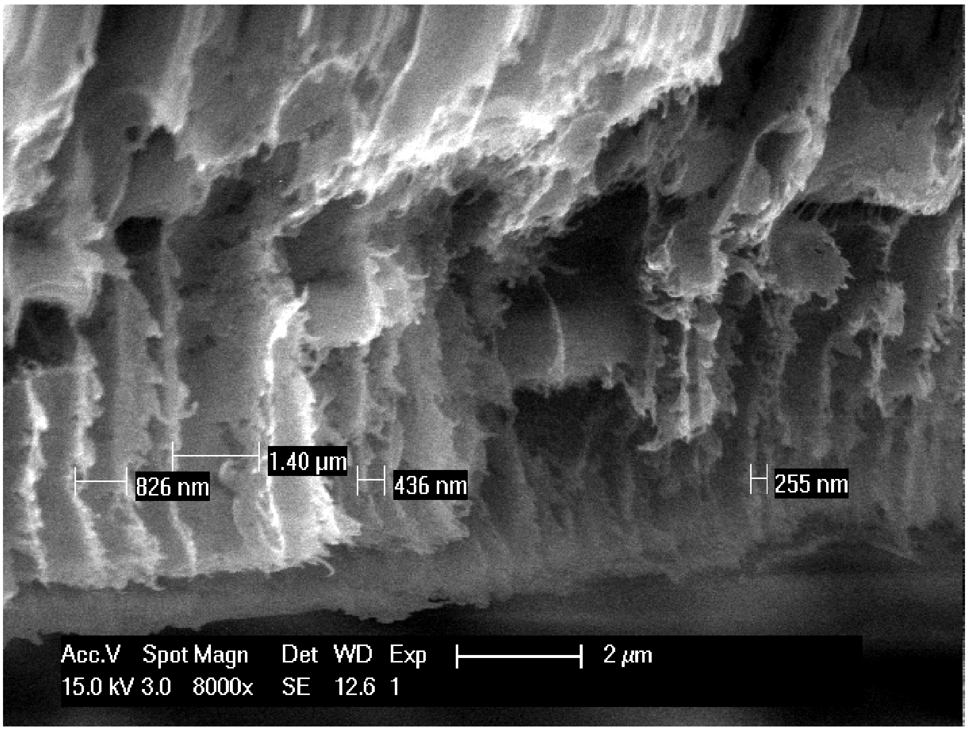


Figure D.4: SEM image of an IND-PS-B sample (magnification 8000x)

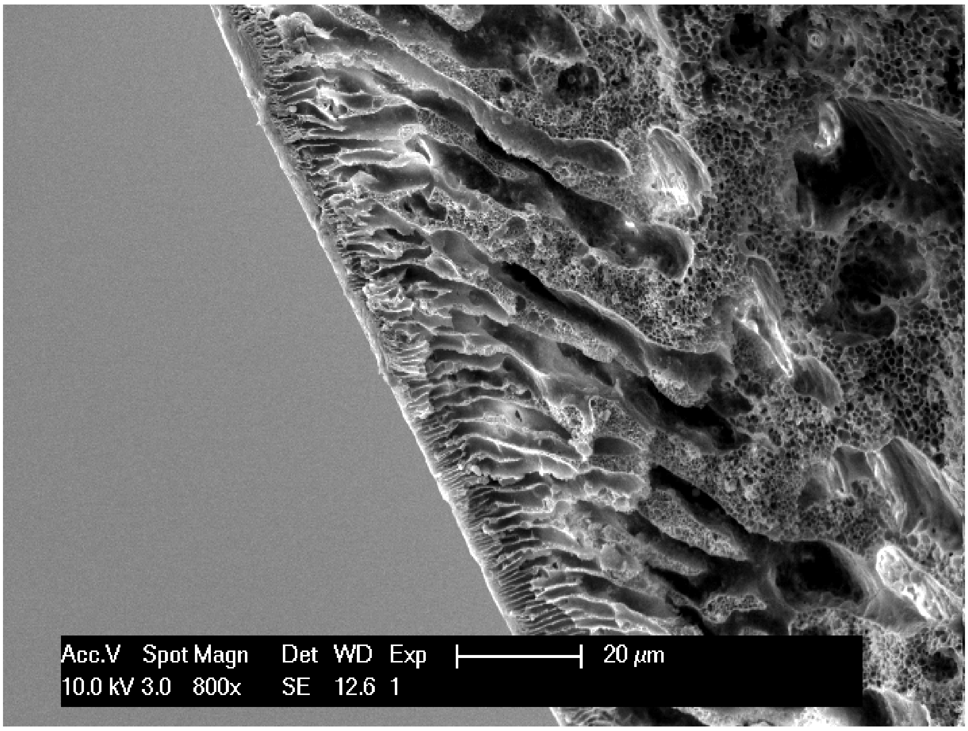


FIGURE D.5: SEM image of an IND-PS-FR sample (magnification 800x)

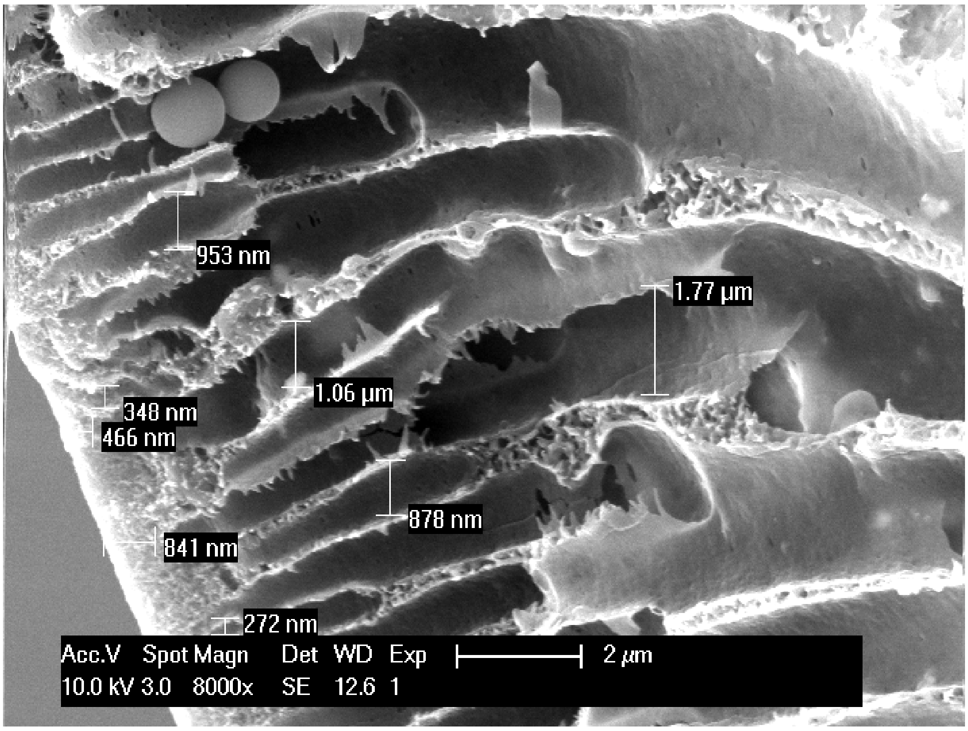


FIGURE D.6: SEM image of an IND-PS-FR sample (magnification 8000x)

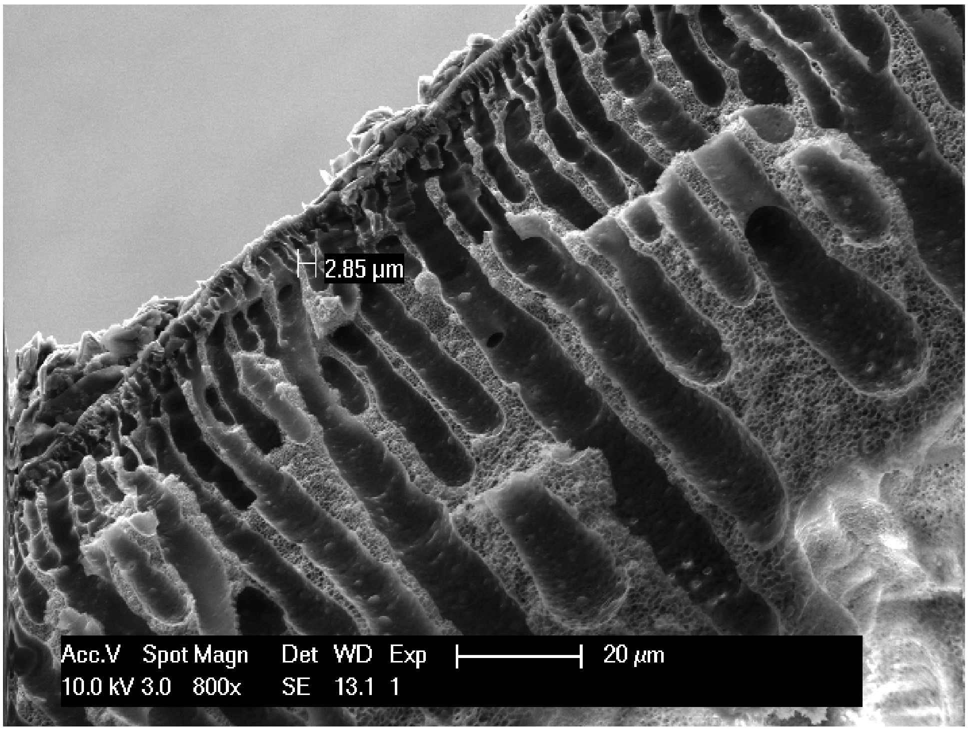


FIGURE D.7: SEM image of an IND-ABS-A sample (magnification 800x)

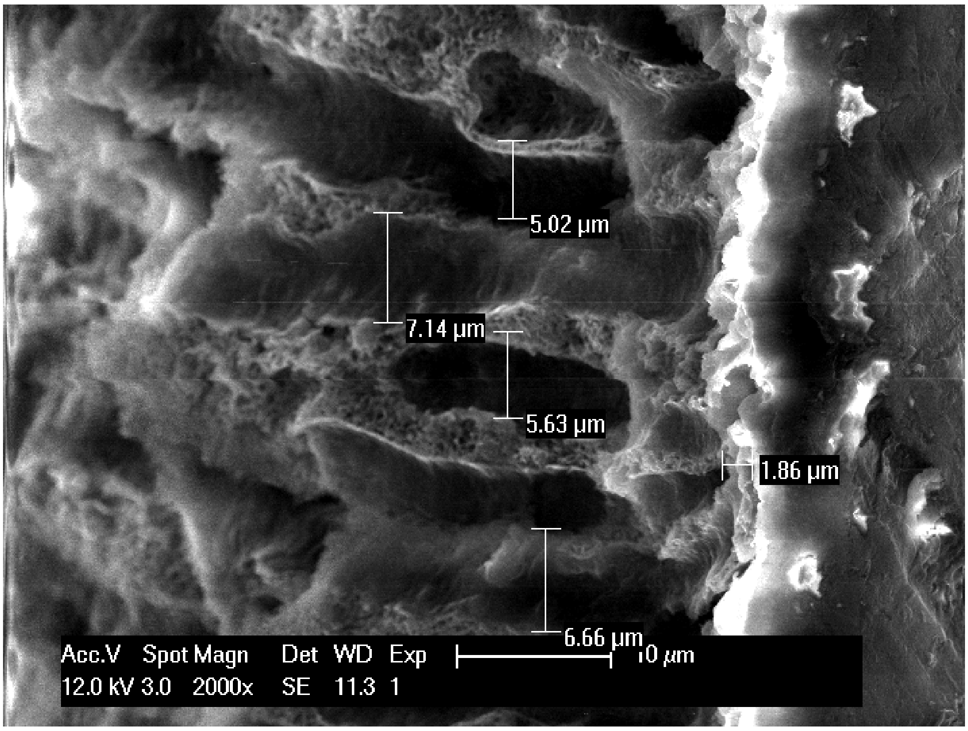


FIGURE D.8: SEM image of an IND-ABS-A sample (magnification 10000x)

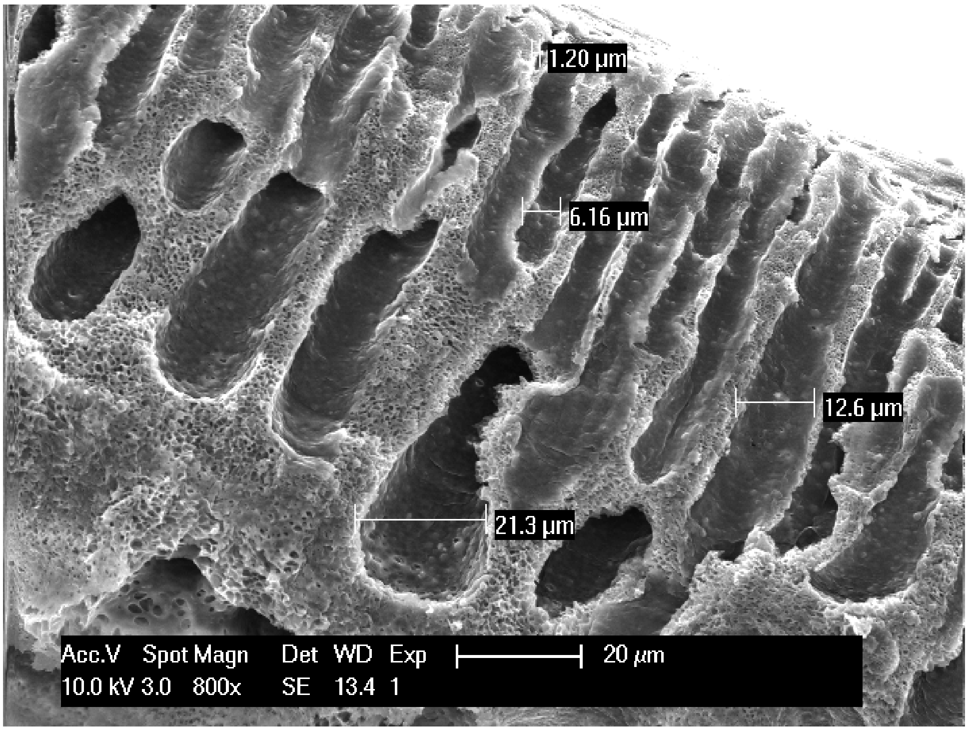


Figure D.9: SEM image of an IND-ABS-B sample (magnification 800x)

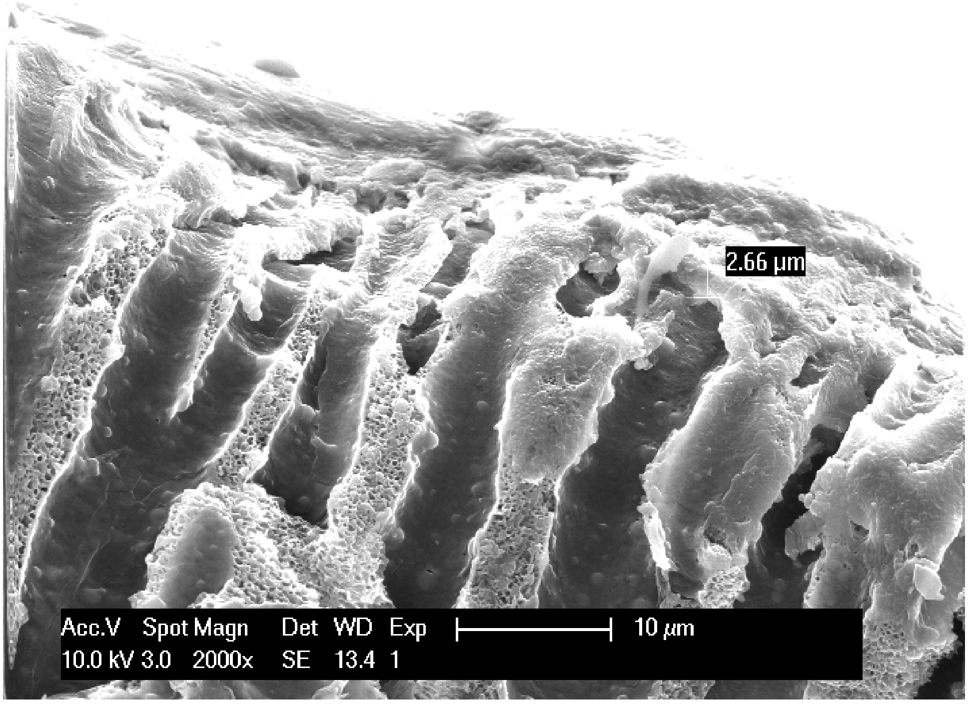


Figure D.10: SEM image of an IND-ABS-B sample (magnification 2000x)

Appendix E

Market & industry analysis

This appendix gives more details about the market and industry analyses. The following sections are included:

1. Market analysis of the market of GreenWater (W&WWT market), including a list of potential direct customers.
2. Industry analysis of the competition of GreenWater (membrane industry), including a list of potential competitors and a price benchmark analysis.

E.1 Market analysis

Very broadly speaking, the customer market of GreenWater is the water and wastewater treatment (W&WWT) industry. The W&WWT industry in the EU is established and mature, and as a consequence it is highly consolidated. Many processes have remained essentially unchanged for decades, though innovation and changes are currently occurring in for example membrane filtration and disinfection. [6]

Water utilities across the EU are often large multinational firms, for example Veolia and Suez. Outside utilities the W&WWT industry consists of a small number of large technology 'original equipment manufacturing' (OEM) firms, for example ITT and Siemens. Besides these large, global companies, there are also many smaller, more locally active, companies [6]. A thorough, yet not exhaustive list is provided below.

The largest component of the W&WWT industry is the production of drinking water, accounting for 43% of treated water usage. In 2010 the global turnover of the W&WWT industry was € 283 billion of which EU turnover accounted for € 94.5 billion. Industry growth is steady at 0.7% annually. The EU is a leading region, with the five largest global companies (Veolia, RWE, Agbar, Suez and SAUR). The United States is home to many of the remaining global leaders (*e.g.* ITT and GE Water). Also Israel and Singapore are becoming increasingly important, driven in part by severe water stress and high population densities. [6]

The direct customers of GreenWater are the OEMs, active in Belgium and the rest of Europe. A comprehensive list (see table E.1) of these companies is composed. OEMs are usually active in different segments of the market. The three identified segments are:

Segment 1: Engineering & consulting services:

1. Process engineering and design of installations.
2. Supply of specific services (no hardware), renting of material.
3. Consultancy, software, modelling.

Segment 2: Construction & supply:

1. Building and/or supply of installations.
2. Contractor for (turn-key) projects or installations.

Segment 3: Operation & financing

1. Co-financing, operation & maintenance.
2. Ownership, public-private partnerships.

The OEMs in the list are assigned one or more of the segments based on their (known) activities. However, this is a simplification since these companies do not always fit in such a sharp classification.

E.2 Industry analysis

The industry in which GreenWater aims to compete is, generally speaking, the membrane industry. The worldwide membrane industry was worth about € 20 billion in 2000, of which sales of membranes and modules represents about 25%. The total market growth has been strong at about 8%-10% annually. This market definition is very broad. A more specific definition is the UF and MF industry - worth about € 1.4 billion in 2000. [23, 25]

Figure E.1 illustrates the end uses of membrane technology. In 2010 there was a global capacity of approximately 27 million m^3/day of treated water produced by membrane filtration plants. Drinking water is the most common output (43%). Desalination, wastewater treatment and membrane bioreactor plants together account for approximately 50% of usage. [6]

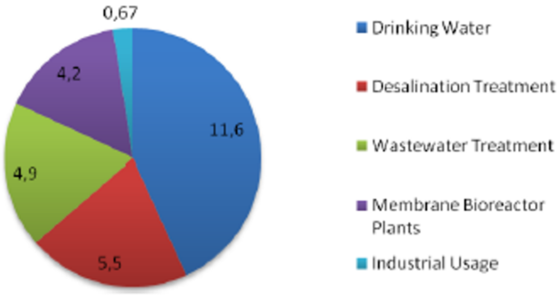


FIGURE E.1: The purpose of membrane and ultrafiltration plants in 2010 (by amount of permeate flow (million m^3/day) [6]

The membrane-based industry is very complex, because it includes a variety of enterprises with different positions in the overall supply chain. Some companies concentrate on the production of membranes and modules only and cooperate with equipment manufacturers

TABLE E.1: List of OEMs active in the W&WWT market in Europe

Company	Active segments	Remarks
Agbar	1, 2, 3	Subsidiary of Suez Environnement
Ageco Environmental Consulting	1	Mainly energy & safety, less activity in W&WWT
BWT Belgium	1, 2	High activity in membrane filtration
Cegelec	1, 2	Less active in membrane filtration
Degrémont	1, 2, 3	Subsidiary of Suez Environnement
Enprotech	1, 2, 3	
Fabricom GTI	1, 2	
GEA Westfalia Separator Belgium	1, 2, 3	High activity in drinking water treatment and material recovery from wastewater
Keppel Seghers Belgium	1, 2, 3	
KH-Engineering	1, 2, 3	
Lenntech	1, 2, 3	
Ronoh	2	Works for example as contractor for Aquafin
RWE	1, 2, 3	Leading EU company
Saur	1, 2, 3	Leading EU company
Siemens	1, 3	Leading EU company
Suez Environnement	1, 2, 3	Leading EU company with high level of vertical integration
Veolia (Belgium)	1, 2, 3	Leading EU company with high level of vertical integration
Waterleau	1, 2, 3	
Welders Filtration Technology	1, 2, 3	

that are often highly specialized in certain applications - as is also the business model of GreenWater. Other companies focus on applications only and use membranes supplied by different manufacturers - these companies resemble the OEMs. [6]

The global market of suppliers of membrane filtration plants is highly consolidated. An illustration of this is that the five largest global membrane suppliers (*i.e.* Pentair X-Flow, GE Water, Siemens, Asahi Kasei and Hyflux) had a combined market share of 91% in 2010 [6]. However, besides these large players, a large amount of small companies exist. A comprehensive, but not exhaustive list of ultrafiltration membrane suppliers is composed in table E.2.

The companies listed in table E.2 represent the most important direct competitors of GreenWater. However, there are also indirect competitors. Such companies do not supply membranes, but supply substitutes (*e.g.* activated carbon suppliers). An analysis of these indirect competitors is out of the scope of this thesis research.

Table E.2: List of membrane suppliers

Company	Country of origin
Amicon/Merck Millipore	USA
Ande Membrane Separation Technology & Engineering	China
AquaSource	France
Asahi Kasei	Japan
Berghof Membrane Technology	Germany
Daicel	Japan
GE Water	USA
GEA Filtration	USA
Hyflux	Singapore
Innovative Membrane Technologies	Netherlands
Kalle Koch Membrane Systems (Abcor)	USA
Membran-Filtrations-Technik (MFT)	Germany
Microdyn-Nadir	Germany
Millipor Nitto Denko	Japan
Novasep	France
Oltremare Membrane Srl	Italy
Para Membranes Co.	South Korea
PCI Membranes (Xylem)	UK
Pentair X-Flow	Netherlands
QUA Group LLC	USA
RisingSun Membrane Technology	China
Shanghai Liquapure Filtration Co.	China
Synder Filtration	USA
TriSep Corporation	USA
Wafilin Systems	Netherlands
CSM (Woongjin Chemical Co.)	South Korea

E.2.1 Price benchmark analysis

To determine a realistic, competitive price it is crucial to look at what the competition is offering. The comprehensive list of UF membrane suppliers of table E.2 can serve as a sample survey for determining a price benchmark. All the suppliers are contacted and obtained, non-confidential price quotes for UF membranes are listed in table E.3. To have comparable figures, all the prices include VAT and are specified for the membrane sheet only, excluding costs for any module, control system, piping, works, *etc.* Also the corresponding membrane type, two membrane characteristics (polymer type and MWCO), and the supplier are listed.

Although not all suppliers disclose price information, a representative number of membrane suppliers and membrane types is obtained. The prices range between € 69/m^2 and € 130/m^2.

Table E.3: Price benchmark for UF membranes

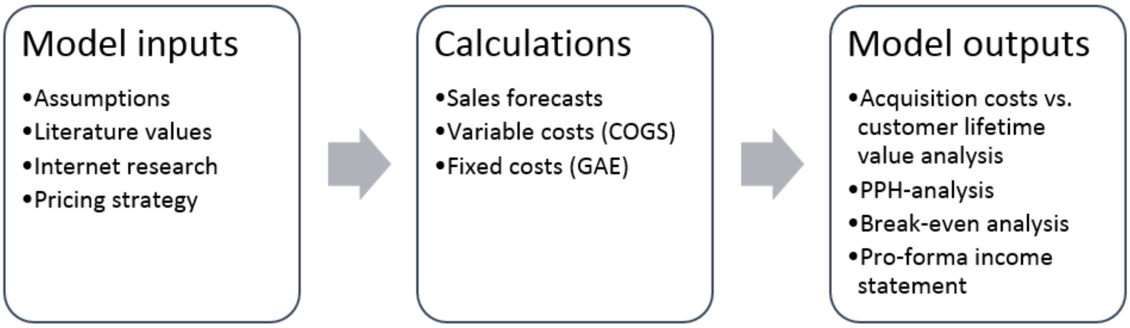
Price	Type	Polymer	MWCO [kDa]	Supplier
€ 93.00/m^2	PES series	PES	1 – 50	Ande Membrane Separation Technology & Engineering
€ 93.00/m^2	PSf series	PSf	20 – 50	Ande Membrane Separation Technology & Engineering
€ 93.00/m^2	PVDF series	PVDF	50 – 100	Ande Membrane Separation Technology & Engineering
€ 114.95/m^2	UP series	PES	5 – 20	Microdyn Nadir
€ 114.95/m^2	UH series	PESH	4 – 50	Microdyn Nadir
€ 130/m^2	Iris series	Not specified	Not specified	Novasep
€ 68.72/m^2	EnciQ UF	PVDF	Not specified	QUA group LLC
€ 69.75/m^2	UE series	PES	5 – 50	RisingSun Membrane Technology
€ 69.75/m^2	US series	PS	20 – 50	RisingSun Membrane Technology
€ 69.75/m^2	UF series	PVDF	50 – 100	RisingSun Membrane Technology
€ 80/m^2	MK30	PES	30	Synder Filtration

Appendix F

Integrated economic model

To perform the necessary business analyses, make sales and costs forecasts, and produce pro forma financial statements for GreenWater, an integrated economic model is developed. This economic model links all the analyses and necessary assumptions in order to obtain consistent results. The economic model is spreadsheet-based, and implemented in Microsoft Excel®.

The model structure is depicted in figure F.1. The inputs of the model are assumptions (rough estimations, literature values, and internet research) and the pricing strategy. All the assumptions are listed in one assumption sheet. The other model input is the pricing strategy. Based on these inputs, sales forecasts and variable and fixed costs forecasts are made. These forecasts form the basis for a number of business analyses (acquisition costs vs. customer lifetime value analysis, PPH-analysis, break-even analysis) and the production of pro forma financial statements for GreenWater (income statement). These analyses and financial statements are used as quantitative basis for the feasibility analysis of the business model (see section 6.2.3).



Model inputs
- Assumptions
- Literature values
- Internet research
- Pricing strategy

Calculations
- Sales forecasts
- Variable costs (COGS)
- Fixed costs (GAE)

Model outputs
- Acquisition costs vs. customer lifetime value analysis
- PPH-analysis
- Break-even analysis
- Pro-forma income statement

Figure F.1: Model structure of the integrated economic model

This appendix provides more details on the following parts:

1. Model inputs: assumption sheet and pricing strategy
2. Model calculations: forecasts for sales and costs
3. Model outputs:
    a. Acquisition costs estimation

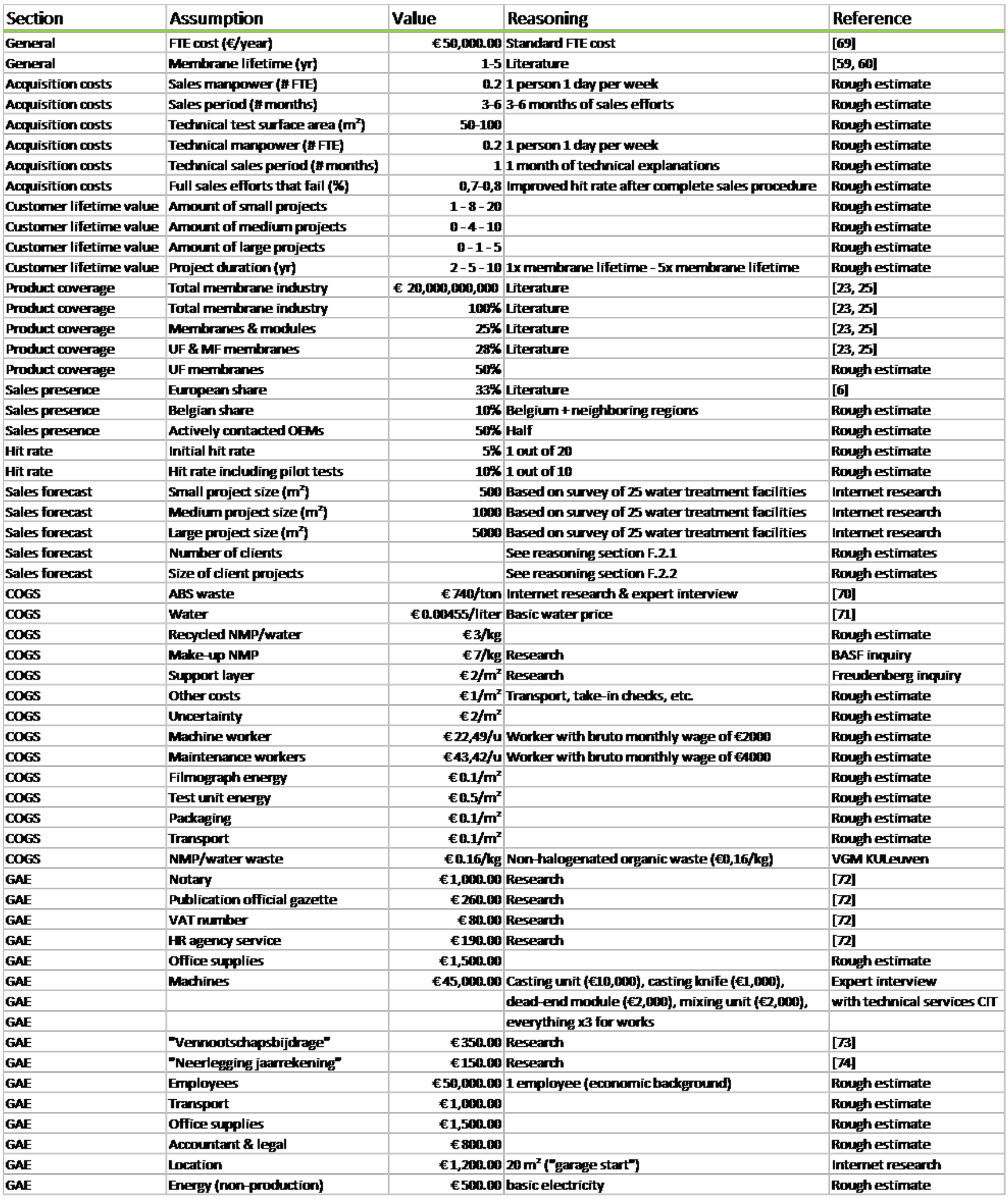
b. Customer lifetime value estimation
c. PPH analysis
d. Three-year pro-forma income statement
e. Break-even analysis

F.1 Model inputs

The model inputs are the assumptions and the pricing strategy. The assumptions are discussed in the next section. The pricing strategy is discussed in section 6.2.3: the price (incl. VAT) is set at € 60/m^2, which results in € 49.59/m^2 (excl. VAT).

F.1.1 Assumption sheet

Naturally, to perform calculations concerning the feasibility, assumptions must be made. For this economic model, the assumptions are based on literature values, internet research, rough estimates, and some expert interviews and supplier inquiries. Figure F.2 contains all the assumptions made in the integrated economic model. The reasoning behind the assumption is given, together with the specific references [6, 23, 25, 59, 60, 69–74].



Section	Assumption	Value	Reasoning	Reference
General	FTE cost (€/year)	€50,000.00	Standard FTE cost	[69]
General	Membrane lifetime (yr)	1-5	Literature	[59, 60]
Acquisition costs	Sales manpower (# FTE)	0.2	1 person 1 day per week	Rough estimate
Acquisition costs	Sales period (# months)	3-6	3-6 months of sales efforts	Rough estimate
Acquisition costs	Technical test surface area (m^2)	50-100		Rough estimate
Acquisition costs	Technical manpower (# FTE)	0.2	1 person 1 day per week	Rough estimate
Acquisition costs	Technical sales period (# months)	1	1 month of technical explanations	Rough estimate
Acquisition costs	Full sales efforts that fail (%)	0,7-0,8	Improved hit rate after complete sales procedure	Rough estimate
Customer lifetime value	Amount of small projects	1 - 8 - 20		Rough estimate
Customer lifetime value	Amount of medium projects	0 - 4 - 10		Rough estimate
Customer lifetime value	Amount of large projects	0 - 1 - 5		Rough estimate
Customer lifetime value	Project duration (yr)	2 - 5 - 10	1x membrane lifetime - 5x membrane lifetime	Rough estimate
Product coverage	Total membrane industry	€ 20,000,000,000	Literature	[23, 25]
Product coverage	Total membrane industry	100%	Literature	[23, 25]
Product coverage	Membranes & modules	25%	Literature	[23, 25]
Product coverage	UF & MF membranes	28%	Literature	[23, 25]
Product coverage	UF membranes	50%		Rough estimate
Sales presence	European share	33%	Literature	[6]
Sales presence	Belgian share	10%	Belgium + neighboring regions	Rough estimate
Sales presence	Actively contacted OEMs	50%	Half	Rough estimate
Hit rate	Initial hit rate	5%	1 out of 20	Rough estimate
Hit rate	Hit rate including pilot tests	10%	1 out of 10	Rough estimate
Sales forecast	Small project size (m^2)	500	Based on survey of 25 water treatment facilities	Internet research
Sales forecast	Medium project size (m^2)	1000	Based on survey of 25 water treatment facilities	Internet research
Sales forecast	Large project size (m^2)	5000	Based on survey of 25 water treatment facilities	Internet research
Sales forecast	Number of clients		See reasoning section F.2.1	Rough estimates
Sales forecast	Size of client projects		See reasoning section F.2.2	Rough estimates
COGS	ABS waste	€740/ton	Internet research & expert interview	[70]
COGS	Water	€0.00455/liter	Basic water price	[71]
COGS	Recycled NMP/water	€3/kg		Rough estimate
COGS	Make-up NMP	€7/kg	Research	BASF inquiry
COGS	Support layer	€2/m^2	Research	Freudenberg inquiry
COGS	Other costs	€1/m^2	Transport, take-in checks, etc.	Rough estimate
COGS	Uncertainty	€2/m^2		Rough estimate
COGS	Machine worker	€22,49/u	Worker with bruto monthly wage of €2000	Rough estimate
COGS	Maintenance workers	€43,42/u	Worker with bruto monthly wage of €4000	Rough estimate
COGS	Filmograph energy	€0.1/m^2		Rough estimate
COGS	Test unit energy	€0.5/m^2		Rough estimate
COGS	Packaging	€0.1/m^2		Rough estimate
COGS	Transport	€0.1/m^2		Rough estimate
COGS	NMP/water waste	€0.16/kg	Non-halogenated organic waste (€0,16/kg)	VGM KULeuven
GAE	Notary	€1,000.00	Research	[72]
GAE	Publication official gazette	€260.00	Research	[72]
GAE	VAT number	€80.00	Research	[72]
GAE	HR agency service	€190.00	Research	[72]
GAE	Office supplies	€1,500.00		Rough estimate
GAE	Machines	€45,000.00	Casting unit (€10,000), casting knife (€1,000),	Expert interview
GAE			dead-end module (€2,000), mixing unit (€2,000),	with technical services CIT
GAE			everything x3 for works	
GAE	"Vennootschapsbijdrage"	€350.00	Research	[73]
GAE	"Neerlegging jaarrekening"	€150.00	Research	[74]
GAE	Employees	€50,000.00	1 employee (economic background)	Rough estimate
GAE	Transport	€1,000.00		Rough estimate
GAE	Office supplies	€1,500.00		Rough estimate
GAE	Accountant & legal	€800.00		Rough estimate
GAE	Location	€1,200.00	20 m^2 ("garage start")	Internet research
GAE	Energy (non-production)	€500.00	basic electricity	Rough estimate

Figure F.2: Assumption sheet of the integrated economic model

F.2 Model calculations

In this section, the forecasts made in the economic model for the sales and costs of GreenWater are discussed.

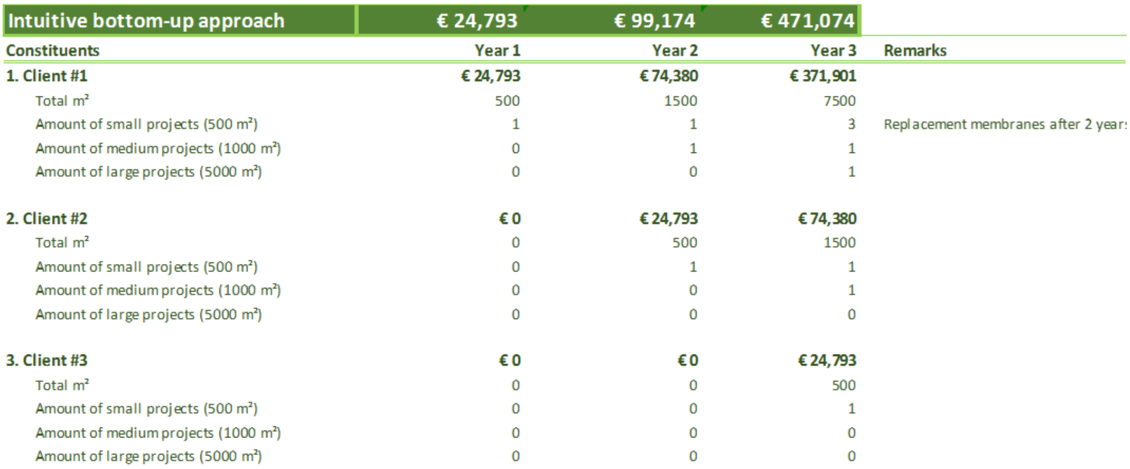
F.2.1 Sales forecast

An intuitive, bottom-up approach to estimate the sales for the first years is to estimate the number of clients and the value of these clients. The assumptions are discussed here and the results are shown in figure F.3.

The first two years are typically slow start-up years: it is conservative not to expect too many sales in this period. For the first year, a conservative estimate is to achieve one client, which allows to produce membranes for one small project (500 m^2). This generates a turnover of approximately € 25,000. For the second year, suppose the first client stays loyal and offers an additional small project and one medium project (1,500 m^2); and suppose a second client is found, bringing in one small project. Altogether, this represents 2,000 m^2 or a modest turnover of approximately € 100,000 for the second year.

After these two initial years, the start-up difficulties are expected to end. The company should have grown and have built up a solid sales experience. Besides, starting from the third year, recurrent membrane replacement revenues are coming in (based on an average membrane lifetime of 2 years). Therefore, in the third year, GreenWater is expected to generate stable revenues. It is assumed that in the third year, the first two clients are retained and are gradually providing more projects, while again another new client is found with one small project. This accounts to a total of 9,500 m^2 and a decent, but conservative € 470,000 in turnover.

A good "gut check" for the turnover of the third year, is to compare it with the results from the PPH analysis (see section F.3.2). PPH analysis is a top-down approach based on the potential market share, and leads to an annual turnover estimation of € 600,000, rising to € 1.2 million if accompanied by successful pilot test results. This is in the same order of magnitude as the turnover estimated for the third year by the intuitive, bottom-up approach; and therefore gives some confidence to the estimated values.



Intuitive bottom-up approach	**€ 24,793**	**€ 99,174**	**€ 471,074**	
Constituents	**Year 1**	**Year 2**	**Year 3**	**Remarks**
1. Client #1	**€ 24,793**	**€ 74,380**	**€ 371,901**	
Total m^2	500	1500	7500	
Amount of small projects (500 m^2)	1	1	3	Replacement membranes after 2 year
Amount of medium projects (1000 m^2)	0	1	1	
Amount of large projects (5000 m^2)	0	0	1	
2. Client #2	**€ 0**	**€ 24,793**	**€ 74,380**	
Total m^2	0	500	1500	
Amount of small projects (500 m^2)	0	1	1	
Amount of medium projects (1000 m^2)	0	0	1	
Amount of large projects (5000 m^2)	0	0	0	
3. Client #3	**€ 0**	**€ 0**	**€ 24,793**	
Total m^2	0	0	500	
Amount of small projects (500 m^2)	0	0	1	
Amount of medium projects (1000 m^2)	0	0	0	
Amount of large projects (5000 m^2)	0	0	0	

Figure F.3: Sales estimation

F.2.2 Costs forecast

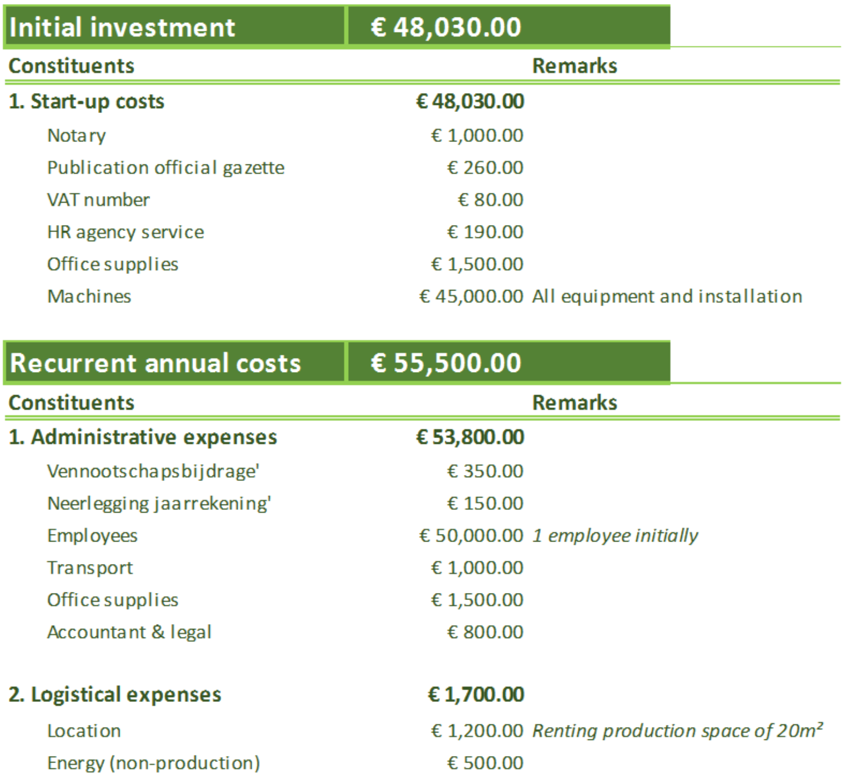
In this section, two types of costs are forecasted: (i) the variable costs or cost of goods sold (COGS) and (ii) the fixed costs, *i.e.* the general and administrative expenses (GAE).

Figure F.4 shows that the COGS are estimated by dividing it into five cost categories: raw materials, workers, energy, packaging, and waste. These are further divided into individual elements. For these individual elements, the costs and amount needed per m^2 membrane surface can be found or estimated more easily. Factored together, the COGS is estimated at € 7.17/m^2 membrane surface. An important assumption in the COGS is the price of plastic waste. For this specific case, the used ABS waste is rather pure and the cost gain in comparison with virgin ABS is only about 30%. However, using waste streams with a low demand (for example EPS waste, which is 98% less expensive than virgin EPS) could provide a more significant cost advantage. It is key to investigate these streams in the future.

Cost of goods sold		**€ 7.17 /m² membrane**	
Constituents			**Remarks**
1. Raw materials		**€ 5.80 /m²**	
ABS waste	740 €/ton	75 g/m²	*Platts Polymerscan (McGraw Hill Financial)*
Water	0.00455 €/liter	0.8 liter/m²	*Research*
Recycled NMP/water	€ 3.00 €/kg	200 g/m²	*Rough estimate*
Make-up NMP	7 €/kg	20 g/m²	*BASF inquiry*
Support layer	2 €/m²	1 m²/m²	*Freudenberg inquiry*
Other costs	1 €/m²	1 m²/m²	Transport, take-in checks, etc.
2. Workers		**€ 0.56 /m²**	
Machine worker	22.49 €/u	1 min/m²	*Worker with bruto monthly wage of €2000*
Maintenance workers	43.42 €/u	0.25 min/m²	*Worker with bruto monthly wage of €4000*
3. Energy		**€ 0.60 /m²**	
Filmograph energy		0.1 €/m²	Rough estimate
Test unit energy		0.5 €/m²	Rough estimate
4. Packaging		**€ 0.20 /m²**	
Packaging		0.1 €/m²	Rough estimate
Transport		0.1 €/m²	Rough estimate
5. Waste		**€ 0.02 /m²**	
NMP/water waste	0.16 €/kg	100 g/m²	*Non-halogenated organic waste (€0,16/kg)*

FIGURE F.4: Estimation of the cost of goods sold

GAE consist of two types: (i) one-off investments and (ii) recurrent annual costs. The one-off investments comprise the purchase of equipment and some typical start-up costs. The recurrent annual costs are divided in (i) administrative expenses and (ii) logistical expenses, and then further in individual costs that can be easily estimated or found in literature. This estimation, depicted in figure F.5, leads to the estimation of a one-off investment of € 48,000 and a recurring € 55,500 annual fixed costs.



Initial investment	**€ 48,030.00**	
Constituents		**Remarks**
1. Start-up costs	**€ 48,030.00**	
Notary	€ 1,000.00	
Publication official gazette	€ 260.00	
VAT number	€ 80.00	
HR agency service	€ 190.00	
Office supplies	€ 1,500.00	
Machines	€ 45,000.00	All equipment and installation

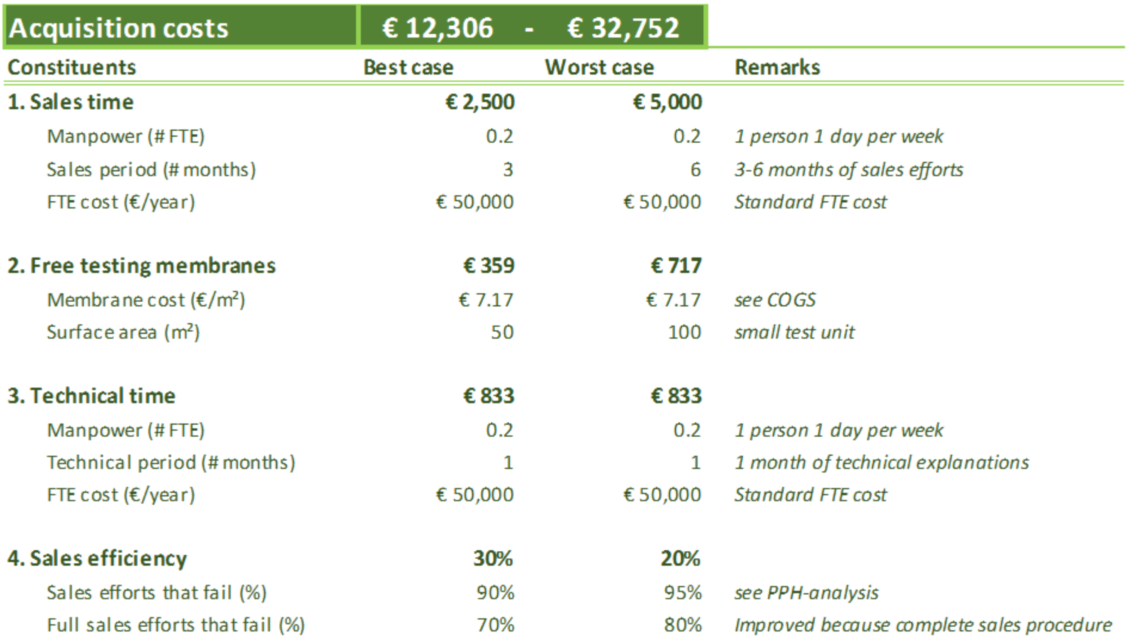
Recurrent annual costs	**€ 55,500.00**	
Constituents		**Remarks**
1. Administrative expenses	**€ 53,800.00**	
Vennootschapsbijdrage'	€ 350.00	
Neerlegging jaarrekening'	€ 150.00	
Employees	€ 50,000.00	*1 employee initially*
Transport	€ 1,000.00	
Office supplies	€ 1,500.00	
Accountant & legal	€ 800.00	
2. Logistical expenses	**€ 1,700.00**	
Location	€ 1,200.00	*Renting production space of 20m^2*
Energy (non-production)	€ 500.00	

FIGURE F.5: Estimation of the general and administrative expenses

F.3 Model outputs

F.3.1 Acquisition costs vs. customer lifetime value analysis

The **acquisition cost** is the total cost to acquire one customer. In figure F.6, the acquisition costs for successful sales procedures are estimated by breaking them down into three constituents: sales time, free testing membranes, and technical time. Besides, it is necessary to also include costs for unsuccessful sales: such sales also induce costs but do not generate revenues afterwards. Therefore, these costs should be included in the cost of the successful sales. This is done via a sales efficiency factor. This factor is chosen higher than the actual hit rate (see section F.3.2), because most unsuccessful sales are already aborted in an early stage, leading to limited costs. The estimation is done for best and worst case scenarios, leading to an estimated acquisition cost of € 12,000 - € 33,000.



Acquisition costs **€ 12,306 - € 32,752**

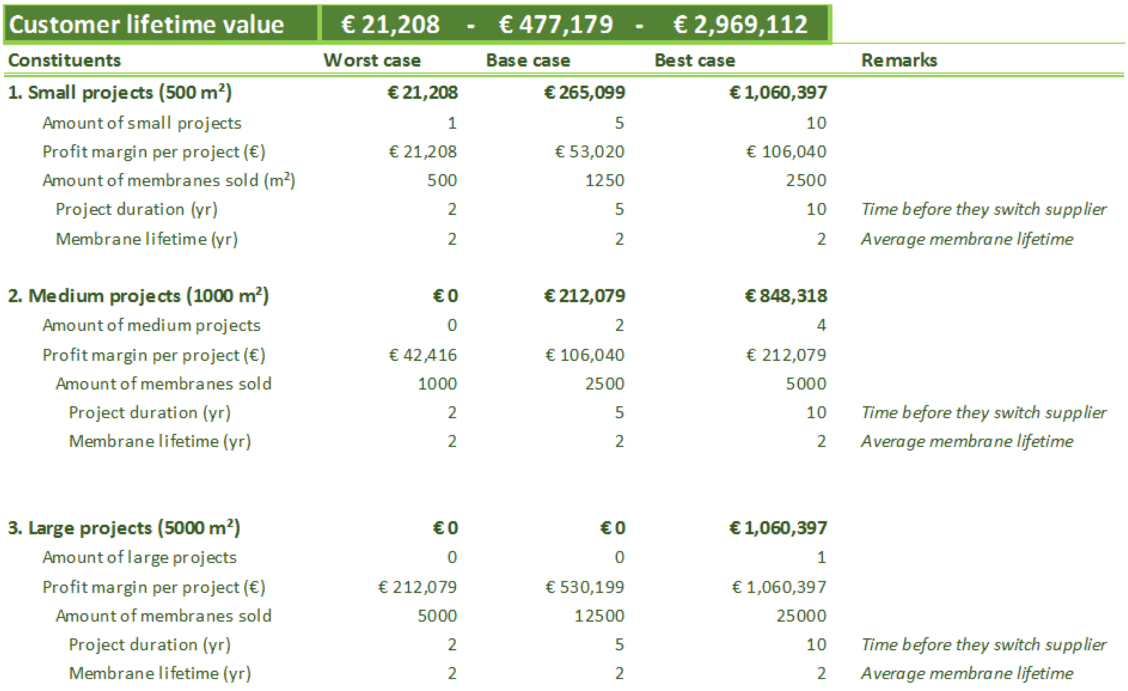
Constituents	Best case	Worst case	Remarks
1. Sales time	**€ 2,500**	**€ 5,000**	
Manpower (# FTE)	0.2	0.2	*1 person 1 day per week*
Sales period (# months)	3	6	*3-6 months of sales efforts*
FTE cost (€/year)	€ 50,000	€ 50,000	*Standard FTE cost*
2. Free testing membranes	**€ 359**	**€ 717**	
Membrane cost (€/m^2)	€ 7.17	€ 7.17	*see COGS*
Surface area (m^2)	50	100	*small test unit*
3. Technical time	**€ 833**	**€ 833**	
Manpower (# FTE)	0.2	0.2	*1 person 1 day per week*
Technical period (# months)	1	1	*1 month of technical explanations*
FTE cost (€/year)	€ 50,000	€ 50,000	*Standard FTE cost*
4. Sales efficiency	**30%**	**20%**	
Sales efforts that fail (%)	90%	95%	*see PPH-analysis*
Full sales efforts that fail (%)	70%	80%	*Improved because complete sales procedure*

FIGURE F.6: Acquisition costs estimation

The **customer lifetime value** is the value a customer, once acquired, brings to the company. This value is estimated in figure F.7, by breaking down one customer into three constituents: small, medium and large projects the customer brings to GreenWater. One OEM has, according to its size, from five to more than twenty projects per year. It is likely that, after a successful sale, the OEM will initially appoint GreenWater one small project (*e.g.* 500 m^2).

In the worst case, the project results do not meet the requirements and the partnership ends after one project. If not, it is likely that GreenWater will be appointed multiple small and large projects over the lifetime of the partnership. Based on this intuitive reasoning, the customer lifetime value is estimated for worst case (€ 21,000), base case (€ 480,000) and best case (€ 3,000,000) scenarios.

Based on both the acquisition costs and the customer lifetime value estimations, their ratio can be determined and analyzed. This is discussed in section 6.2.3.



Customer lifetime value **€ 21,208 - € 477,179 - € 2,969,112**

Constituents	Worst case	Base case	Best case	Remarks
1. Small projects (500 m^2)	**€ 21,208**	**€ 265,099**	**€ 1,060,397**	
Amount of small projects	1	5	10	
Profit margin per project (€)	€ 21,208	€ 53,020	€ 106,040	
Amount of membranes sold (m^2)	500	1250	2500	
Project duration (yr)	2	5	10	*Time before they switch supplier*
Membrane lifetime (yr)	2	2	2	*Average membrane lifetime*
2. Medium projects (1000 m^2)	**€ 0**	**€ 212,079**	**€ 848,318**	
Amount of medium projects	0	2	4	
Profit margin per project (€)	€ 42,416	€ 106,040	€ 212,079	
Amount of membranes sold	1000	2500	5000	
Project duration (yr)	2	5	10	*Time before they switch supplier*
Membrane lifetime (yr)	2	2	2	*Average membrane lifetime*
3. Large projects (5000 m^2)	**€ 0**	**€ 0**	**€ 1,060,397**	
Amount of large projects	0	0	1	
Profit margin per project (€)	€ 212,079	€ 530,199	€ 1,060,397	
Amount of membranes sold	5000	12500	25000	
Project duration (yr)	2	5	10	*Time before they switch supplier*
Membrane lifetime (yr)	2	2	2	*Average membrane lifetime*

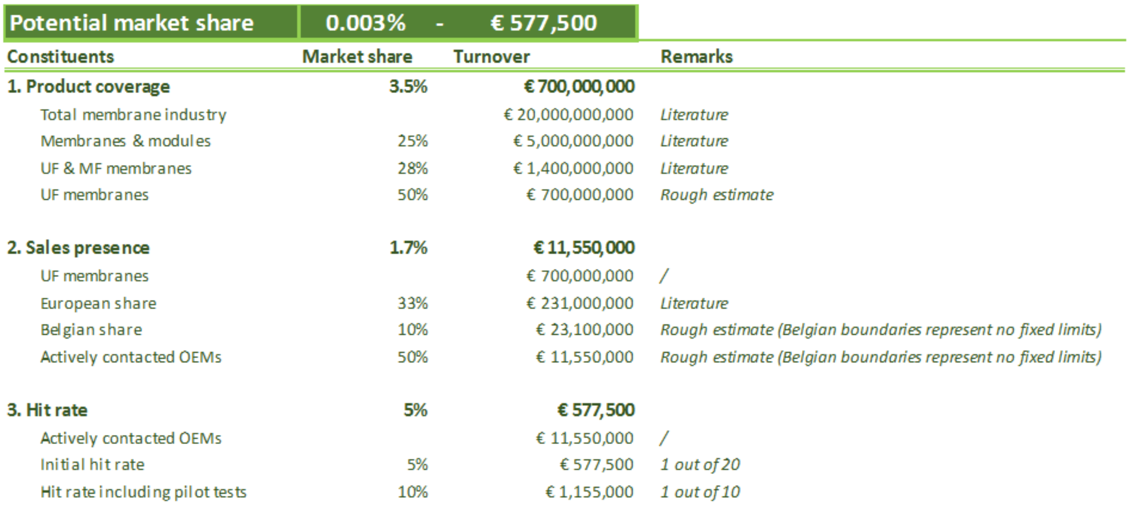
FIGURE F.7: Customer lifetime value estimation

F.3.2 PPH analysis

PPH-analysis allows to estimate the potential market share by dividing it into three factors [63]:

$$Market\ share = (product\ coverage \cdot sales\ presence \cdot hit\ rate) \cdot total\ market\ size$$

The product coverage (3.5%), sales presence (1.7%), and hit rate (5-10%) are estimated in figure F.8 by dividing them into their respective constituents. Based on these estimates and the size of the total membrane industry (€ 20 billion), the preliminary estimate for the annual turnover is € 600,000, rising to € 1.2 million if accompanied by successful pilot test results.



Potential market share	0.003%	€ 577,500	
Constituents	**Market share**	**Turnover**	**Remarks**
1. Product coverage	**3.5%**	**€ 700,000,000**	
Total membrane industry		€ 20,000,000,000	*Literature*
Membranes & modules	25%	€ 5,000,000,000	*Literature*
UF & MF membranes	28%	€ 1,400,000,000	*Literature*
UF membranes	50%	€ 700,000,000	*Rough estimate*
2. Sales presence	**1.7%**	**€ 11,550,000**	
UF membranes		€ 700,000,000	/
European share	33%	€ 231,000,000	*Literature*
Belgian share	10%	€ 23,100,000	*Rough estimate (Belgian boundaries represent no fixed limits)*
Actively contacted OEMs	50%	€ 11,550,000	*Rough estimate (Belgian boundaries represent no fixed limits)*
3. Hit rate	**5%**	**€ 577,500**	
Actively contacted OEMs		€ 11,550,000	/
Initial hit rate	5%	€ 577,500	*1 out of 20*
Hit rate including pilot tests	10%	€ 1,155,000	*1 out of 10*

Figure F.8: PPH analysis

F.3.3 Pro forma income statement

The economic model produces a three-year income statement for GreenWater. This is shown in figure 6.3 in section 6.2.3.

F.3.4 Break-even analysis

The economic model produces a break-even analysis for GreenWater, shown in figure 6.4 in section 6.2.3.

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