

Designing Porous Polymer Systems for Water Treatment Applications

by

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Author's Declaration

This thesis consists of materials of which I authored or co-authored: see Statement of Contributions included in the thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Statement of Contributions

Chapter 3 of this thesis is adapted from a published manuscript “**Styrene-ethylene-butylene-styrene (SEBS) melt-blown fibers for oil spill remediation and oil barrier geotextiles**”, **Polymer, 298, 126942** in which I am the first author. Shreeja Gupta, a co-op student in Dr. Mekonnen’s group, assisted in the carrying out of some experiments, the creation of figures, and aided in the preparation of the draft manuscript. Research associate Binh-Minh Trinh offered significant guidance in designing experiments, as well as creating figures and reviewing the manuscript prior to submission. Dr. Mekonnen, who conceptualized the project, provided valuable guidance and supervision throughout the process, in addition to reviewing the manuscript.

Chapter 4 of this thesis is adapted from a manuscript, “**3D-printed, flow-through water filters for microplastic capture: the effect of surface porosity, column height, and pressure-sensitive adhesives on removal efficiency**”, that is currently in the final stages of preparation for submission, in which I am the first author. Dr. Mekonnen initiated the project, provided guidance and supervision, in addition to reviewing the manuscript.

Abstract

Increasing pollution and contamination of the World's water bodies come with great concern over potable water safety and accessibility. Current solutions for water treatment often have large carbon footprints or are too expensive to scale up effectively. These shortcomings warrant the exploration of new and effective methods of water treatment. Polymer-based solutions offer lightweight, scalable, and inexpensive methods for water filtration while being minimally intrusive to the surrounding environment. In particular, porous polymeric materials have garnered considerable attention due to their high specific surface area, which enables them to have enhanced interactions with their target analyte.

This thesis presents two such types of porous materials: nonwoven fabrics and three-dimensional (3D) printed filters. The first section of this thesis focuses on nonwovens, a type of fabric comprised of bonded, interlocking, randomly oriented fibers. Nonwovens can be used as topically placed sorptive mats for the removal of pollutants, or as a pass-through filter for the separation of water from the pollutants. Here, the unique oil gelation properties styrene-ethylene-butylene-styrene (SEBS) block copolymer are leveraged for the creation of melt-blown nonwovens for oil-water separation applications. The poor processability of SEBS, due to its elastomeric nature, was overcome through highly optimized processing parameters to create fine diameter, highly porous nonwoven mats. These mats possessed exceptional lipophilicity and oil-water separation properties due to the oil-soluble midblocks of SEBS that created a semi-solid gel capable of retaining all oil it came into contact with.

The latter section of this thesis focuses on 3D printing, specifically fused deposition modelling (FDM), for the creation of flow-through filters for microplastic capture. 3D-printed parts are often very smooth, greatly limiting their surface area and ability for microplastics to become lodged on their surface. To overcome this, a sacrificial additive was added to the base polymer matrix that could be etched out, creating a highly porous surface that greatly improved the filtration efficiency of the printed filters. Pressure-sensitive adhesives (PSAs) were also explored and were found to further bolster the filtration capabilities of the filters. This is due to the added tack and non-covalent interactions that more strongly hold microplastics to the surface of the filters. The findings from these studies demonstrate a promising direction for utilizing porous polymer systems in water treatment applications.

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Dedication

I want to dedicate this work to all of my family members who have always shown me blind and unconditional love and support. A very special thank you to my wonderful parents, who have always gone above and beyond to help and support me in my pursuit of my goals and dreams. There is no way I could have done it without you. Thank you to my grandparents, who have helped me financially throughout university and welcomed me home whenever I had the chance. Thank you to my sister Maggie and my cousin Gwyneth for being my home away from home while I'm in Waterloo. I always enjoyed getting to see you and follow your journeys here at UW.

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List of Abbreviations/Nomenclature (Alphabetical)

2D	Two dimensional
3D	Three dimensional
ABS	Acrylonitrile butadiene styrene
AM	Additive manufacturing
ATR	Attenuated total reflectance
CAD	Computer-aided design
CLIP	Continuous liquid interface production
CV	Coefficient of variation
DCD	Die-to-collector distance
DIPS	Diffusion induced phase separation
DIW	Direct ink writing
DLP	Digital light printing
DSC	Differential scanning calorimetry
FDM	Fused deposition modeling
FTIR	Fourier transform infrared spectroscopy
GO	Graphene Oxide
H_{cc}	Heat of cold crystallization
LVR	Linear viscoelastic region
MFI	Melt flow index
MOF	Metal-organic framework

MW	Molecular weight
NC	Nanoclay
OCA	Oil contact angle
P2EHA	Poly(2-ethylhexyl acrylate)
PA	Polyamide/nylon
PC	Polycarbonate
PDA	Polydopamine
PE	Polyethylene
PEEK	Polyetheretherketone
PEG	Polyethylene glycol
PEGDA	Polyethylene glycol diacrylate
PEKK	Polyetherketoneketone
PETE/PET	Polyethylene therephthalate
PHEMA	Polyhydroxymethyl methacrylate
PHR	Parts per hundred resins
PLA	Poly (lactic acid)
PMMA	Polymethyl methacrylate
POM	Polarized optical microscope
PP	Polypropylene
PS	Polystyrene
PSA	Pressure sensitive adhesive

PVC	Polyvinyl chloride
SBS	Styrene-butadiene-styrene
SEBS	Styrene-ethylene-butyl-styrene
SEM	Scanning electron microscope
SLA	Stereolithography
SLS	Selective laser sintering
T_{cc}	Cold crystallization temperature
T_g	Glass transition temperature
THF	Tetrahydrofuran
TIPS	Thermally induced phase separation
T_m	Melt temperature
TPE	Thermoplastic elastomer
UV	Ultraviolet
WCA	Water contact angle
ΔG_m	Gibbs free energy of mixing

Chapter 1– Introduction

1.1 Motivation

Water is the World's most valuable resource. It sustains all life on Earth, and its monetary value is immeasurable. Only 3% of all water on Earth is freshwater, and of that 3%, 0.06% of it is readily accessible for human consumption [1,2]. Therefore, it is imperative that we take great care of the little potable water we have access to. But with the population continuing to grow, and industry growing to match, the amount of pollutants finding their way into lakes and river is reaching alarming levels [3]. Heavy metals, pesticides, petroleum, dyes, microorganisms, pharmaceuticals, and microplastics are but a few of the pollutants making their way into our waterways [4–10]. These pollutants can lead to a wide variety of health problems and complications in people [11], as well as having disastrous effects on ocean biodiversity and ecosystems [12].

Many technologies and systems have been created for the treatment of polluted water. They can broadly be categorized into physical methods (filtration, sedimentation, distillation), chemical methods (coagulation, flocculation, chlorination), and biological methods (bacteria, microbes) [13]. The efficacy and cost of these techniques as a whole are variable, and their utilization is usually dependent on the pollutant being targeted in the situation. Many of them require large wastewater treatment plants to be scaled up properly, which have extremely high capital costs associated with their construction.

Polymers are a very broad class of macromolecule that are characterized by their chain-like structure of repeating (monomer) units. Plastics, a common polymer in society, have seen

continued growth for solving problems since after the Second World War in the 1950's [14]. Their desirability stems from their lightweight, inexpensive, and highly tunable properties. All of these traits make polymers a good candidate to use as a building block for more affordable, scalable, and easily usable solutions to the water pollution crisis. A large number of polymers and processing techniques have already been explored for water filtration [15–19], however more research is still needed to improve efficiency, scalability, cost, and environmental impact.

1.2 Research objectives

The aim of this thesis is to explore different polymers and methods of polymer processing for the improved filtration of water pollutants. Two separate scientific studies were carried out and the results reported on. In both studies, a different polymer and polymer processing technique was utilized, both thoroughly investigating how the material behavior and its method of preparation can be leveraged for water filtration applications.

The first part of the research focuses on the creation of melt-blown extrusion of nonwoven mats fabricated from SEBS block copolymer for oil-water separation and oil spill remediation. The goal of this work was to highly optimize the processing parameters of the melt blowing setup in order to overcome the poor processability of SEBS associated with its low melt strength and low MFI. The fabricated SEBS nonwovens were then rigorously tested to examine their capability to selectively absorb oil from contaminated water systems.

The second part of the research focuses on the modification of 3D-printed PLA filters in order to maximize their ability to capture microplastics from wastewater. The goal of this work was to investigate several different parameters: surface porosity, surface interaction, and filtration

column height, to observe their contributions to improved removal efficiency. Sacrificial plasticizer etching was examined for its ability to create fine micro and nanopores on the filter surface. Two different PSAs were examined for their ability to further bolster the adhesion of microplastics. Flow-through filtration was undertaken to demonstrate a more hands-off and facile method for filtering the wastewater compared to attempts made in literature.

1.3 Thesis outline

The subsequent sections of the thesis are structured as follows: Chapter 2 provides a literature review that focuses on topics relating to the creation of porous polymer materials and the types of pollutants found in water and wastewater. Chapter 3 presents the completed research work on melt blown nonwovens for oil-water separation and remediation, which includes a detailed fabrication process, characterization, and demonstration of application. Chapter 4 covers the complete experimentation, characterization, and utilization of 3D-printed, PSA-coated, etched, flowthrough filters that can be used for microplastic capture. Finally, Chapter 5 provides the overall conclusions and recommendations that can be drawn from this thesis.

Chapter 2: Literature Review

2.1 Introduction

Freshwater, the world's most basic and vital resource for human survival, is also one that has become more and more precious as the population continues to increase. It is estimated that roughly 4 billion people experience water scarcity at least one month a year, and about 2.2 billion people do not have access to safe drinking water [20,21]. The scarcity of water, which used to be an issue mostly associated with arid regions such as Africa and the Middle East where resources are more limited, has now extended to the "developed world" due to increased industrial, agricultural, and domestic needs in populous areas [22]. Regardless of whether the water issues are due to quantity or quality, the result is insufficient water to maintain a healthy population and ecosystem.

A large hurdle to the global water crisis is the uptick in pollutants and contaminants in all waterbodies across the globe, making obtaining fresh potable water one step more difficult. With less than 0.0067% of Earth's water available for human consumption [23], we must collectively seek to preserve what little we do have. Water contaminants come in all shapes and sizes, with each one presenting different challenges for efficient, safe, and cost-effective removal during water treatment.

a) Organics

All pollutants comprising of carbon, as well as hydrogen, oxygen, nitrogen, and/or sulphur are considered organic pollutants. This can pertain to an extensive number of compounds found in

human-generated waste such as industrial and agricultural wastewater, as well as sewage and wastewater from urbanization [24].

b) Inorganics

Non-carbon-based pollutants can be generically classified as inorganic pollutants. These include heavy metal ions like lead and arsenic, mineral acids like sulfuric and hydrochloric acid, and mineral salts like nitrates, nitrites, fluorides, and ammonium. Agricultural wastewater is a large contributor to inorganic pollution due to the many nitrogen-based entities present in fertilizer, as well as pesticides that will often contain heavy metals and toxic salts like ferrous sulfate[25,26]. Municipal and industrial sewage can generate many of the same pollutants. Some, like nitrites, are well known carcinogens [24].

c) Radioactives

Radioactive materials can leech into water bodies from both natural and manmade sources. Many radioactive pollutants exist within the Earth's crust and dissolve into surface drinking water through underground reservoirs etc. As well, testing of nuclear devices and poorly regulated power plants can also produce radioactive materials. Uranium, thorium, aluminium, radium, and radon, all of which are linked to various cancerous, toxic, and mutagenic effects, are the most common radioactive pollutants [24,27,28].

d) Suspended solids

While most of the previously mentioned contaminants are either soluble or at least miscible in water, suspended solids interact with water but retain their solid state. This can include both

organic (decayed matter) and inorganic (clay, sand, sediment) suspensions, and to varying degrees of stability [24]. Another popular type of suspended solid that has seen a large increase in research recently is microplastics and nanoplastics [29–32]. These microplastics pose a significant threat to aquatic life and subsequently the food chain due to their ability to adsorb other harmful pollutants like heavy metals and organic contaminants. They also persist in nature for a very long time, meaning they bioaccumulate and cause increased harm over time as concentrations increase [29].

e) Pathogens

Bacteria, viruses, and parasites are all pathogens that can be present in wastewater. Standing waste water reservoirs and ponds give these pathogens ideal environments to flourish. Some common pathogens include Hepatitis, Norwalk virus, Salmonella, Vibrio cholera, Cryptosporidium, Cyanobacteria, Echoviruses, Schistosoma, etc., all of which can lead to gastrointestinal illness [24,33].

f) Thermal Pollution

Thermal power plants can generate increases in local aquatic systems by 10 °C [24]. Studies have shown that variations in mean temperature by as little as 2 °C were enough to generate 30% habitat loss for local species [34].

Many technologies and systems have been developed over the years in an effort to reclaim as much polluted and contaminated water as possible. The most traditional method is the use of physical forces for contaminant removal. Screens of varying mesh sizes from 0.001mm to 6+mm capture suspended particulates which are later cleaned and the waste captured can be

disposed of properly. In locations where handling screens is impractical, comminutors, large rotating cutters, break down large floating debris while also combating wastewater stench and perception. Flow equalization combines physical stirring and dilution to equalize factors such as flow rate, pollutant concentration, and temperature for more sophisticated down stream processes. Sedimentation aims to collect large, settled particles at the bottom of a reservoir. In contrast, flotation aims to use air bubbling to force particles to the top of a reservoir for collection [35,36]. While the installation and upkeep costs of these processes are usually inexpensive, they are severely limited in their efficiency, as well as the range of pollutants that can be targeted.

Biological wastewater treatment methods uses microorganisms and biological pathways to break down and eliminate pollutants from water. Algae, bacteria, microbes, and even fungi can be used in biodegradation to break down pollutants into small molecules that pose little to no threat to macroorganisms. Aerobic biological processes, which produce CO_2 , water, and biomass, include methods such as activated sludge, membrane bioreactors, and sequential batch reactors. Conversely, anaerobic processes, such as anaerobic filters and sludge reactors, produce CO_2 , methane, and biomass. While the potential bonus of biogas production and more energy-efficient process of anaerobic treatment is sometimes desirable, the ease and stability of aerobic treatments makes them more often seen for municipal and household applications [36].

Chemical processes interact with pollutants on a molecular level to bring about some form of change to make them easier to remove or eliminate them altogether. Chemical precipitation,

using carefully selected precipitating agents, causes solids (precipitates) to form that can more easily be separated during a later sedimentation process [37]. The use of chemicals in sedimentation procedures has shown to increase removal by 25-65%, as well as allowing for the removal of previously unremovable contaminants [35]. Adsorption, a hybrid physico-chemical process, can selectively draw soluble substances from wastewater to adhere to a solid surface. Materials like activated carbon have both a high specific surface area and a cheap manufacturing cost, making it desirable for adsorption-driven media. Disinfection selectively destroys unwanted microbes and pathogens that fester in wastewater. Heat, radiation, and chemicals like chlorine, calcium hypochlorite, and ozone are all used in disinfection processes [35,36]. The caveat, however, is that chemical processes are almost always used in conjunction with physical or biological processes. Subsequently, it means that more chemicals end up in the final water, which can greatly reduce its overall reusability.

All of these avenues of water treatment have performance and cost-related shortcomings, which is why they are often used in conjunction with one another. One strain of technology that has gained significant interest in recent years due to its high pollutant removal capabilities and tailorable designs is functional membrane-based systems [38]. Specifically, polymer-based membranes and media offer scalable, economical, and tunable solutions to many water treatment applications. While polymer membranes are not a new technology, dating back to the 1960's and earlier for the transport of gases, filtration, pervaporation, etc. [39,40], it is a still rapidly evolving area due to its breadth and modality.

2.2 Porous polymer technologies

2.2.1 Phase inversion membranes

Phase inversion membranes, also referred to as anisotropic membranes, are a conventional method of membrane preparation first demonstrated by Loeb and Sourirajan in the 1960's when they precipitated a cellulose casting solution in water. Still a very commercially relevant technique used today, phase inversion membrane technology has been applied to over 40 different polymers for different applications [40]. Phase inversion membranes are synthesized by precipitating a polymer out of solution into a solid membrane. Different mechanisms for inducing phase inversion of the polymers include:

- a) Thermally induced phase separation (TIPS) decreases the temperature of the polymer solution to induce precipitation.
- b) Diffusion induced phase separation (DIPS) focuses on the removal of the polymer solvent via diffusional mass exchange. Immersion precipitation draws the solvent out of the polymer solution and replaces it with a nonsolvent that causes the membrane to rapidly precipitate. Vapor adsorption subjects the solution to a nonsolvent-laced gaseous vapor, with the adsorption of the nonsolvent to the polymer causing precipitation. Solvent evaporation relies on the instability of a volatile solvent mixed with a less volatile solvent and the polymer to generate precipitation through preferential evaporation.

More than one method of precipitation can occur in the creation of phase-inverted membranes.

The most important factors to consider with TIPS synthesis is the glass transition temperature

(T_g) of the polymer, the gelation point of the solution, and the thermodynamic interactions between the polymer, solvent, and nonsolvent described by Gibbs free energy of mixing.

$$\frac{\Delta G_m}{RT} = n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_1 \phi_2 \chi \quad (1)$$

NIPS synthesis is more reliant on thermodynamics and is governed by the Flory-Huggins theory for Gibbs free energy of mixing:

$$\frac{\Delta G_m}{RT} = \sum_{i=1}^3 n_i \ln \phi_i + g_{12}(u_2) n_1 \phi_2 + g_{13} n_1 \phi_3 + g_{23}(v_2) n_2 \phi_3 \quad (2)$$

with

$$u_2 = \frac{\phi_1}{\phi_1 + \phi_2}, \quad (2a)$$

$$v_2 = \frac{\phi_2}{\phi_2 + \phi_3}, \quad (2b)$$

where the subscripts 1, 2, and 3 correspond to nonsolvent, solvent, and polymer, respectively, n_i and ϕ_i are the number of moles and volume fraction of each component i , g_{ij} is a binary interaction parameter between components i and j [40].

Both methods highlight an underlying drawback of phase inversion membranes from a cost and sustainability perspective, which is the large amounts of solvent and nonsolvent that are required. Other techniques listed below produce less waste and less harmful waste than phase inversion membranes, however, the pore sizes that can be achieved are amongst the finest that can be fabricated using polymer systems.

2.2.2 Additive manufacturing

Additive manufacturing, also known as 3D printing, works as its name suggests and adds material to the membrane layer by layer. The structure of the 3D printed membrane is designed in a CAD software, sliced into 2D layers, and then translated into a G-code file that tells the printer how to print each layer at a time. The majority of 3D printing techniques are polymer processing techniques, allowing for versatility in material selection based on the application [38].

2.2.2.1 Fused deposition modeling (FDM)

Fused deposition modeling (FDM) has become the face of 3D printing to the general public thanks to its ability to produce sophisticated parts quickly and cost-effectively. FDM works by feeding thermoplastic filaments through a nozzle that heats it and allows it to be extruded on to the build plate. Once the first layer has been printed, the nozzle raises/build plate lowers, allowing the next layer to be printed. Due to the three-dimensional nature of the process, supports or scaffolds of the same material, or a designated support material, are often incorporated into the print code to ensure the stability of segments that would otherwise span large unsupported areas [41]. These supports are easily removed at the end of the print and ultimately allow for a limitless number of designs and architectures to be realized. Another upside of FDM printing is the wide range of materials that can be used. Polylactic acid (PLA), acrylonitrile butadiene styrene (ABS) are two of the most popular from their tuned thermal, rheological, and physical properties, which make them ideal for printing. Other plastics like

polyethylene (PE), polypropylene (PP), polyamide/nylon (PA), polyetheretherketone (PEEK), polyetherketoneketone (PEKK), and polyethylene terephthalate (PETE) [42].

2.2.2.2 Direct ink writing (DIW)

Another extrusion-based technique similar to FDM is direct ink writing (DIW). Polymer solutions are extruded through a needle in a paste-like consistency. Further solidification is usually driven through the evaporation of the solvent or some other solvent-based interaction. DIW is very useful in applications where a conductive membrane is necessary, as these polymer inks often have excellent electrical properties [43]. Due to their lower viscosity, the rheological properties of DIW inks are even more important to ensure ease of flow needed for high quality prints [38]. DIW's ability to print at ambient temperature presents many unique opportunities for applications that require intact optical properties or have heat sensitive entities like cells or biological cultures present in the polymer matrix [44]. The drawback to extrusion-based printing is largely mechanical. The print nozzle size and precision of motor movement by the printer both severely limit to what degree the final print product can be machined [44,45]. Extrusion-based prints usually range from 50-200 μm in precision [46]. Extrusion-printed parts also tend to display anisotropic physical properties due to the preferential programming and alignment of polymer chains while in the molten state [47–49].

2.2.2.3 Selective laser sintering (SLS)

Selective laser sintering (SLS) is a different approach to 3D printing that utilizes high-energy lasers to sinter thin layers of polymer powder together. The build bed starts empty and at a

temperature below the melting temperature of the polymer, with a large material feed reservoir next to it. Resin is fed to the build bed in thin layers, which are then selectively sintered together before the next layer of powder is added. This process repeats until completion, then the part is sieved and shaken to remove the excess powder [50]. This technique negates the need for rheological properties and is instead dictated by the particle size of the powder, layer thickness, and laser intensity. The absence of flow during processing leads to more isotropic physical properties compared to those of extrusion-based 3D printing. However, the reheating of layer boundaries to create proper fusion can lead to thermal anisotropy from layer to layer [51]. Common polymers for SLS printing include PA, polystyrene (PS), thermoplastic elastomers (TPEs), PP, and polycarbonate (PC) [50]. The accuracy of SLS is similar to that of extrusion-based prints, ranging from 80-250 μm [51,52].

2.2.2.4 Vat photopolymerization

Vat photopolymerization is a branch of 3D printing that includes subcategories such as stereolithography (SLA), digital light printing (DLP), and continuous liquid interface production (CLIP). All subcategories leverage the same principle of utilizing photosensitive liquid monomer resins. When a UV light source comes into contact with the photoinitiators in the resin, it promotes the rapid polymerization of the surrounding monomers, making it a similar process to SLS printing [53]. DLP shines a UV light from a digital projector, curing the entire layer of resin simultaneously. The print bed then lowers slightly in the resin bath to allow for the next layer of curing. This makes DLP one of the fastest 3D printing techniques available. The accuracy of the photomasks used in DLP allows for a resolution of roughly 1

μm , much smaller than previously mentioned methods [54]. SLA functions very similarly to DLP, except a UV laser is used instead of a UV projector. The build plate sits one layer height below the surface of the resin bath, the resin is selectively cured to the build plate, then the build plate lowers by another layer thickness and the process is repeated [38]. The resolution of SLA printing varies from 25-50 μm in the XY plane, and 50-100 μm in the Z direction. This is mostly limited by the optical diffraction capabilities of the printer, as well as the absorbance of the resin formulation being used [55]. Transparent polymer resins are very important to the functionality of vat photopolymerization techniques. These resins can be engineered for a given application by varying the content of monomers, oligomers, photoinitiators, and other additives present in the formulation. Acrylate-based resins such as polyhydroxymethyl methacrylate (pHEMA), polyethylene glycol diacrylate (PEGDA), and polymethyl methacrylate (PMMA) are among the most common resins used. However, epoxy-based resins can be used in high performance and high temperature applications, and polyurethane-based resins can be used in flexible applications [56,57].

2.2.2.5 FDM printing control

As previously stated, FDM is currently the most widely used and widely studied method of additive manufacturing. It is also the most traditional in the way it mimics simple polymer melt extrusion. The balance with FDM printing comes down to producing extremely small and well-defined features while ensuring it maintains sufficient mechanical properties to hold together for its designated application [58].

2.2.2.5.1 Layer thickness

In FDM, the 3D design is sliced into thin layers and printed layer by layer. Therefore, each layer has some small thickness, usually between 0.17 mm – 0.3 mm [59]. Thinner layers means that more layers will need to be printed to complete the print, thus increasing your overall print time. Chadha et al. found that for varying infill geometries, increasing layer thickness improved the ultimate tensile strength of the print [60]. This is due to weak interlayer adhesion seen in FDM, since the heat from the molten polymer is insufficient to promote true integrated polymer chain diffusion and entanglement from layer to layer [61]. So, by increasing the thickness of each layer and subsequently decreasing the number of times the print has to rely on weak interlayer fusion, the tensile strength of the print is improved. Another study found contradictory evidence of this; however, they attribute the increase in mechanical properties to increased interlayer adhesion area [62]. **Figure 2.1** is an adapted representation of their findings to show how layer height affects the interlayer adhesion and therefore its associated mechanical properties. Therefore, perhaps a balance between the number of layers and contact area between layers is optimal. However, by increasing layer thickness, you will lose precision in the z-direction and small features in that direction will become less distinguishable.

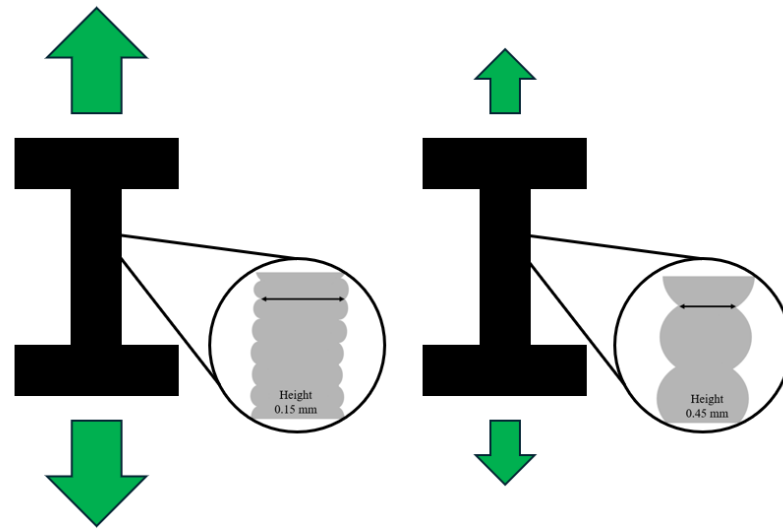


Figure 2.1: The effects of print layer height on mechanical properties. The tensile strength decreases from left image to the right image due to reduced interlayer adhesion area [62].

2.2.2.5.2 Infill density and pattern

3D prints, when not required for high-performance applications, can be manufactured partially hollow. The walls, or visible part of the print, remain the same, while the inside of the print can be printed with just enough polymer that it can support the remaining layers above it.

Figure 2.2 shows some of the infill patterns that are commonly employed, as well as visualization to how infill pattern adjusts as the infill density is increased. Some common patterns that are missing from this figure include gyroid, Hilbert, archi, octa, 3D honeycomb, rectilinear, lines and hexagonal patterns [63,64]. In fact, while the triangular and honeycomb patterns have long been considered the strongest infill pattern due to strong reinforcement and load dispersal [65], more recently the gyroid pattern has been surging in popularity. Due to its constant curvature in all directions, it has no planes of symmetry and therefore no straight lines where maximum stress is usually observed. This allows it to withstand the largest stress for a

given volume of all infill densities [63]. As for infill density, it has been widely agreed upon that higher infill densities produce greater tensile and flexural results, and that the overall mechanical strength of the print is mostly dependent on the total mass of the specimen for all printable polymers [59,66].

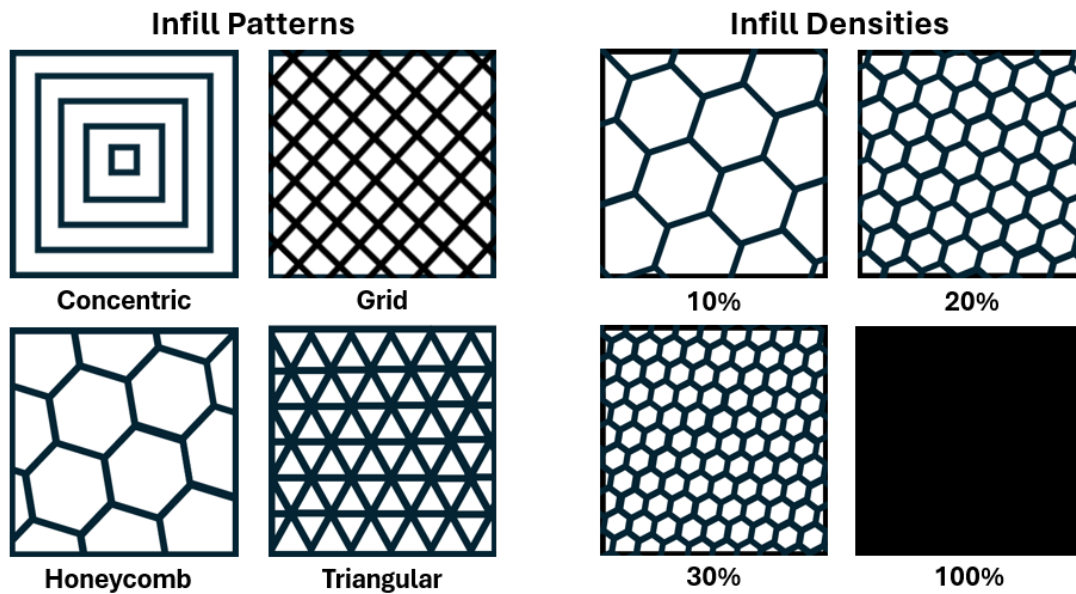


Figure 2.2 A visual representation of commonly used infill patterns, as well as how the patterns change as the infill density increases [64].

2.2.2.5.3 Print speed and temperature

The speed and temperature at which the 3D printer prints a given design will have many effects on the final properties of the print. Molten filaments are viscoelastic fluids with complex internal structures whose mechanical properties hinge on the entanglements and orientations of the polymer chains they're comprised of [67]. While in the molten state, the properties of FDM filaments should be viscously dominated, however there will still be an elastic

component that plays an important role in their behaviour. Increased print speed will put greater stress on the polymer melt as it is drawn out of the barrel faster. This greater stress will pull on the entangled polymer chains, causing them to stretch and align in the direction of the print path [68]. This orientation improves mechanical properties in the print path direction, as the covalent bonds from the polymer chains are stronger than the intermolecular forces and entanglement that were otherwise reinforcing the structure [69]. Higher temperatures will also improve mechanical properties by increasing molecular mobility, making it easier for chains to unentangle and align in the print direction. As well, higher temperatures will promote stronger welds between layers by heating the previous layer by greater amounts, allowing for easier and longer molecular migration and entanglement before dropping below its glass transition temperature again. This phenomenon is known as polymer sintering [69,70]. However, these changes to the internal structure of the polymer melt also have the capability to generate flow instabilities in the extruded filament. While the exact cause of some instabilities is debated, insufficient temperature while drawing the filament too quickly can create phenomena such as “sharkskin”, “stick-slip”, or “melt fracturing” [71]. Beyond this, die swelling and die necking can also occur. Die swelling occurs when a polymer melt is pushed through a die hole too quickly relative to its temperature, giving it insufficient time to relax. When the polymer then comes out of the die nozzle, the chains recoil, causing the filament to swell larger than the die hole [72]. This reduces the precision and capability of the printer to capture small features, as well as potentially mess with the desired layer height of the print. Necking is essentially the opposite problem, where the print speed is too quick relative to how fast the printer is feeding filament through the melting zone. With insufficient flowability, the

polymer drawn from the print nozzle stretches from the stress applied by the already printed polymer stuck to the print bed. It causes for the printed filament to have a smaller than intended diameter [72]. This can lead to air gap voids in between rasters, greatly reducing the mechanical properties of the print and also producing undesired layer heights [69]. Both of these issues can be mitigated with increases in temperature, as it pushes the polymer melt closer to its viscous nature and further from its elastic nature by reducing viscosity and increasing the molecular mobility of the polymer chains. These issues can also both be solved by striking a good balance of the feed rate of the printer and the draw rate or printing speed of the printer. This ensures that an appropriate amount of polymer is being supplied and dispensed from the print nozzle for the duration of the print.

2.2.2.5.4 Build orientation and raster angle

The build orientation of a 3D print refers to which plane will act as the base during the print. The face(s) of the print on this plane will be flush with the print bed and the rest of the print will be constructed upwards. For many builds there will be clear and obvious side that will best serve as the base during the printing process. Some factors to consider are which orientation will have the greatest contact area with the print bed, what orientation will minimize the number of layers required for printing, what orientation will minimize the need for supports and scaffolds, and what orientation will generate the properties needed in the given locations. Greater contact area with the print bed will make your print more stable, making it less likely for a printing error to occur at taller layers where swaying forces could be more prevalent. Paired with this is choosing an orientation that limits the overall height of the print, once again

limiting the chance of a print error at higher layer numbers by eliminating those higher layers entirely. Keeping those factors in mind, reducing material costs should also be considered from an efficiency and economic standpoint. Build orientations that reduce or eliminate the need for supports or scaffolds to structurally aid while printing will almost always be preferable for their feasibility and lack of post-processing to remove the supports [73].

Related to build orientation and the most important consideration in the determination of print design positioning is the raster angle of the print. The raster angle is defined as the angle between the x-axis and the nozzle path during an FDM print. The raster angle is an incredibly important parameter for the reasons outlined when discussing print speed and temperature. Due to the molecular reinforcement from the chains being aligned along the print path, the direction of the print path (the raster angle) has large implications for the mechanical strength of the print. The raster angle should orient towards the direction where the most tensile stress will be experienced. For a build that experiences stress in the x-direction, a raster angle of 0° is best. For stress in the y-direction, a raster angle of 90° will perform better. For stress in the z-direction, perhaps a different print orientation would orient the print in a way that would allow for a good raster angle to support the build better. This was shown when raster angles of 0° , 45° , and 90° were tested on tensile bars pulled in the x-direction. Tensile properties worsened from 0° to 90° as the direction of the print path strayed further from the direction of the tensile force [74]. It is also noted that this shift in raster angle is also a shift in the dominant force bearing the tensile force. Strong covalently bonded backbones from the polymer chains

can bear loads much greater than the weak intermolecular forces and polymeric sintering between layers that bear the complete load by the time a raster angle reaches 90° [75].

2.2.2.5.5 Print bed temperature

The print bed temperature is a unique aspect of 3D printing in that it has two major purposes. It has to both hold and support the print build throughout the entirety of its manufacturing process, as well as determine the rate at which the fabricated print cools as the rest of the print finishes. It could be likened to the mould used in injection molding or blow molding, but in both of those cases, the product is created nearly instantaneously instead of over a relatively long duration. Benwood et al. [76] showed that for PLA tensile bars, increased print bed temperatures led to an increase in density, tensile strength, and tensile modulus. The increase in density can be attributed to higher temperatures promoting longer cooling times. The printed filament will remain viscous for longer, allowing it to properly relax and diffuse into existing voids and form a stronger and higher surface area contact with its neighbouring rasters. This density increase will improve the tensile strength and modulus, but the other contributing factor as the build plate temperature increases, is increased crystallinity of the final fabricated samples. They reported an increase from 1.48% crystallinity with a 45 °C bed temperature to 18.30% crystallinity at a 105 °C bed temperature. This large increase is due to significantly delayed cooling, providing a longer time for crystalline domains to form before cooling below its glass transition temperature (T_g), as well as potentially improved crystallization kinetics from higher chain mobility since PLA is known for its slow crystallization [77]. However, researchers have voiced concerns over the replicability of these levels of control over

crystallinity and crystallization kinetics in real-world applications [78,79]. It is not unreasonable to picture FDM prints one metre or larger. And with polymers being known thermal insulators [80], the ability for heat to conduct up from the print plate to where the new print layers are being applied will be hindered. This could potentially result in anisotropic degrees of crystallinity from the bottom of the print to the top.

2.2.2.5.6 Crystallinity

Polymer crystallinity refers to the amount of a polymer matrix that has three-dimensional order. This order is achieved through the successive folding over of the polymer into sheets known as “lamellae” in regions where molecular mobility is high enough for this to be achieved, while also not so high that the intermolecular forces are disrupted by heat or solvent interactions [81,82]. Crystalline domains are much more densely packed, leading to lower permeability and higher rigidity [82,83]. Improvements in crystallinity correlate to improvements in mechanical properties, as the crystalline domains contribute additional intermolecular interactions that resist applied force [83]. Therefore, the ability to control the crystallinity of a printed structure gives improved control over the printed structure’s mechanical properties.

One method of improving crystallinity in 3D prints is through a post-processing heat treatment or annealing. By heating the final print back above its T_g , the polymer matrix is given additional time to reorder into lamellae, which are thermodynamically favourable, increasing the final degree of crystallinity [84]. This process is referred to as recrystallization [85]. Yang et al. [83] showed that by applying a heat-treatment process on PEEK-CF composites ranging from

slightly above its T_g of 143 °C to just below its melt temperature (T_m) of 343 °C over a 2-hour period, the degree of crystallinity of the sample increased with increasing temperature. This increase in crystallinity then directly translated to improved tensile and flexural moduli values.

Ambient temperature and build plate temperature also play a large role in the degree of crystallinity achieved. While some specialty printers can control the ambient temperature surrounding the print [85,86], many rely on the build plate to provide heat to the print after it exits the print nozzle [87–89]. As discussed above, the time it takes for a print to cool below its T_g , as well as the rate at which it cools down, both impact the final degree of crystallinity. Higher external temperatures, whether ambient or from the build plate, both promote higher degrees of crystallinity in the final print [76,85].

Nucleating agents are another method of controlling the crystallinity of FDM prints. Nucleating agents are additives added to the polymer matrix that increase the number of sites available for crystal formation, or by lowering the energy barrier required for their creation, and thus help to induce quicker and higher levels of crystallization in polymer composites [90,91]. These are especially useful in semi-crystalline polymers and polymers with slow crystallization kinetics, such as industrially popular PLA [92]. Nucleating agents that lower the energy barrier for crystal formation are homogenous nucleating agents, and heterogenous nucleating agents supply sites for crystal domain formation. As the name suggests, homogenous nucleating agents produce more uniform and evenly distributed nucleation but do so less efficiently than their heterogenous counterparts [93]. They can, however, provide value in applications where solid particle fillers are not an option, such as when the polymer matrix

is chemically altered during processing. Sorbitol is one such example of a homogeneous nucleating agent [94]. Heterogeneous nucleating agents provide significantly improved speed and efficiency in the nucleation process, but at the cost of uniformity, making them preferable in applications where crystallization is time-limited [93]. Some examples of fillers that act as heterogeneous nucleating agents are talc [95], silica [96], nanoclay [97], silver nanoparticles [98], and carbon nanotubes [99], to name a few.

2.2.3 Nonwovens

Nonwoven fabrics are an established class of porous materials which are classified as “any structure produced by the bonding or interlocking of randomly oriented fibers, or both, accomplished by mechanical, chemical, thermal, or solvent means and the combination thereof [100].” Nonwovens are desirable for membrane applications due to their extreme ease of fabrication and tunability. After initial preparation, calendaring can be done to tune the thickness, density, pore size, and permeability of the nonwoven for the given application. The fiber diameter, pore size, and thickness are the key factors to consider when determining a nonwoven’s perspective ability to function as a membrane [101].

2.2.3.1 Spun bonding

Spun bonding is an extrusion-based technique in which molten polymer is drawn out of a die with the assistance of high velocity air into a single, fine, continuous filament. The air flow further stretches this filament as it is carried to a collector belt where it is deposited. As more filament randomly deposits on the collector belt, a nonwoven pattern begin to form, held

together by a vacuum suction holding the filament to the belt. All of these steps are similar to that of traditional melt spinning techniques. The final step, the bonding step, consolidates this web of fibers together to an entangled nonwoven mat through the use of mechanical, thermal, or chemical means. Mechanical means uses needles that penetrate the fabric at up to 2200 times/min to promote further entanglement of the collected filament to generate one solid entangled mat. Thermal means, the most common method of bonding, use a hot calendar to press and partially melt crystalline regions together to create a continuously bonded mat [102,103]. The cross-sectional diameters of spunbonded fibers typically range from 15-35 μm , but can vary depending on the polymer used. Good polymers for spun bonding have high molecular weight and a broad molecular weight distribution, giving them higher melt strength and molten ductility. Isotactic PP is commonly used due to its low density and cost, providing the highest value in fibers per kilogram. Polyesters can be used in applications requiring higher tensile strength, modulus, and heat stability. Similarly, PA (nylon-6) has been used due to its exceptional strength, resilience, dyeability, and low rigidity [103].

2.2.3.2 Melt blowing

A technology similar to that of spun bonding is melt blowing. Thermoplastic polymers are extruded through a die at high temperatures onto a collector. The difference between the two is that melt-blown fibers are forcibly launched out of the die with the aid of hot, high velocity air injected at the end of the die to attenuate the filaments into shorter, smaller diameter fibers often ranging from 0.5-4 μm in size [101,104]. The collector is located closer to the die, meaning that thermal annealing between fibers occurs on impact and that a secondary bonding

step is not required. Melt-blown nonwovens are generally softer, fluffier, and weaker than spunbonded fabrics due to their decreased fiber diameter and lack of secondary processing to improve interfabric bonding.

However, the significant drop in fiber diameter leads to a much greater specific surface area (SSA) in melt-blown nonwovens compared to spunbonded nonwovens. This, when paired with the high porosity of melt-blown nonwovens, makes them usable for medical garments and PPE, wound dressings, thermal insulation, automotive components, drug delivery, geotextiles, and filtration applications, to name a few [105–108]. The hydrophobic nature of many common thermoplastic nonwovens, such as PP nonwovens, has been demonstrated to make melt-blown nonwovens useful in oil sorption applications. Poor interactions with water due to low surface energy means that high selectivity and high sorption oil spill remediation can be realized [109,110].

2.2.3.2.1 Melt blowing setup

Typical melt-blowing setups all consist of the same components: a polymer feed, metering pump, die assembly, air assembly, and rotating fiber collection and transference system [111]. In the extrusion-based process, first the feed stock must be fed through the hopper into the solids conveying zone of the extruder. As the polymer moves from the conveying zone to the melting zone and finally to the melt pumping zone, the pellets/resin are converted to a molten polymer melt through conduction heating and mechanical shearing and friction from the rotating screws of a standard twin screw extruder. The screws are also designed in such a way that the amount of shear applied increases from zone to zone and the polymer becomes less

viscous. In the melt pumping zone, a metering pump is present to monitor the amount of pressure coming from the extruded polymer and use that to control the flow rate of the molten polymer out of the die. This is crucial in the creation of uniform melt-blown fiber diameters. The metering pump factors in variables such as temperature and viscosity to deliver fixed volumes of polymer per unit of time. The polymer then exits the extruder through the die assembly, which is essentially responsible for the entire creation of the melt blown fibers. The die pathways will split and narrow, creating hundreds of holes for the polymer to exit from across the face of the die. As the polymer exits the die holes, it is further stretched and attenuated into long fine fibers by very hot high-velocity air (generally 230 °C – 260 °C and 170 m/s – 275 m/s) [112]. The attenuated fibers are shot through the air until they collide with a rotating collector. Due to the semi molten consistency of the fibers upon impact with the collector, the fibers will self adhere to each other. Post-collection calendaring can be optionally done to control final nonwoven mat thickness and density. A considerable number of factors and parameters play a role in this quick but complex polymer processing technique. Therefore, many digital and physical experiments and research has been carried out to better understand the physical phenomena of melt blowing [113–115].

2.2.3.2.2 Fiber motion

Whipping is an aerodynamically driven phenomenon where the polymer fibers undergo lateral oscillations as they come into contact with the highly turbulent and high-velocity air streams coming out of the die nozzle [113]. This theory was first proposed by Entov and Yarin [114], who proclaimed that if the velocity of the flow exceeds a certain critical value, any additional

disturbances in the flow will grow and generate instability. Xie et al [116,117] have conducted both theoretical and experimental research into measuring these turbulent fluctuations. Simulations found that the 5 cm on either of the centerline experienced significant turbulence fluctuations, as well as the highest velocity air flow as molten polymer exited the die. They also found that the intensity of the whipping action increased with increased distance from the die, while the frequency of whipping actions decreased with increased distance from the die. This quantification and simulation of turbulent flow is important to provide proper understanding of the behaviour of the polymer during fiber creation.

Xie et al have also examined another important parameter for determining the motion of fibers out of the die which is the geometry of the die itself. Two main geometries are used in industry are the slot die and annular/swirl die. The slot die has a rectangular orifice where the air converges from either side and the polymer is extruded out of the middle of the rectangular opening. Xie et al conducted a three-dimensional analysis of the air field flow out of a slot die with the use of an anemometer and controllable motor. They were able to show that air flow was significantly reduced near the edge of the slot die face, making the air field not an even plane. This means that factors such as the whipping motion experienced, degree of attenuation, entanglement, and cooling will all change at the corners of the die, affecting both fiber size and strength. The instantaneous speed and temperatures experienced greater fluctuations as distance from the die increased, which can lead to whipping and prevent a smooth draft as it approaches the collector [116].

Annular dies, sometimes referred to as swirl dies, are known for producing a swirling airflow that can subsequently produce helical fiber motion and therefore unique fiber geometries. The inner wall of the annular die can produce a variation of turbulent effects, such as the formation of a recirculation region due to there being an interaction with both the center wall near the die exit. This is much more turbulence than is experienced by the slot die [118]. A study on the relationship between the lateral swirling diffusion of airflow and the resultant fiber distribution showed that there exists a critical distance from the die where helical motion is essentially unaffected by the swirling velocity of the air. However, it was also found that the boundary for lateral diffusive air velocity had a major impact in controlling the lateral fiber distribution on the collection screen [119].

2.2.3.2.3 Fiber diameter control

2.2.3.2.3.1 Melt flow index (MFI)

Perhaps the most important variable in melt-blown nonwovens is the diameter and diameter distribution of the resultant fibers in the nonwoven mat. As one would probably expect, there are a large number of factors that can influence the final diameter of melt-blown fibers. Perhaps the most important parameter is melt flow index (MFI), a value that is inversely correlated with viscosity which describes the rate at which the polymer melt can flow through a standardized hole at a given load and temperature in a ten-minute span [120]. MFI is expressed in the units of grams per 10 minutes. High MFI polymers will flow easier in the melt-blowing setup and are more easily attenuated by the hot air, leading to finer diameter melt blown fibers [121]. The MFI of a polymer is affected by factors such as temperature, molecular weight

(MW), and the introduction of additives like fillers and plasticizers [122,123]. All of these factors relate back to the degree of entanglement and mobility experienced by the polymer chain in the melt. Since increasing temperature leads to increased operational costs during production and occasionally unwanted polymer degradation, polymer melt composition is often the place for making changes to achieve the desired MFI. Switching to lower MW variations of the polymer can easily improve MFI without the need for any other changes, however the mechanical properties of the produced nonwoven mat will suffer due to reduced molecular entanglements.

Plasticizers, often small polymers themselves, are additives that help to improve flexibility and decrease crystallinity by reducing the amount of intermolecular interactions between polymer chains [124]. They do this by penetrating into the free volume of the polymer matrix and forming bonds with the polymer chains while not interacting with themselves, making it easier for the polymer chains to slide over each other in a molten state [125]. Therefore, increased plasticizer content will improve the MFI of a polymer. Plasticizers can be categorized as either internal or external. External plasticizers are what are most often mixed in as an additive to polymer composites and blends. They are able to interact with the polymer chains, disrupt polymer interactions, and increase the free volume of the composite. They are, however, not chemically bonded to the polymer matrix, so they are more susceptible to evaporation and separation [126]. Internal plasticizers are, inversely, a component of the actual polymer, either through co-polymerization or through a secondary reaction. They operate similarly to external plasticizers in that they aim to reduce molecular interactions through an increase in free volume

and improvement in chain mobility, except they accomplish this through bulky structures covalently bonded to the backbone or side chains of the polymer [127]. Some plasticizers seen in modern processing techniques include glycerol, polyethylene glycol (PEG), epoxidized soybean oil, and citrates [125,128–130]. Traditionally, phthalate-based plasticizers are also a very popular option for plasticization in polymers like polyvinyl chloride (PVC), however some have been phased out in recent years due to health concerns [129,131].

On the flip side, fillers are small particles added to polymer matrices to interact with and ultimately stiffen the resulting composite. Fillers can do this by acting as nucleating sites for crystal growth and producing higher crystallinity in the polymer matrix. However, at higher concentrations, fillers can also hinder chain movement and arrangement [132]. Therefore, size, concentration, morphology, and interfacial interactions are important to consider when selecting an appropriate filler for a given application [133]. As an example, an organic filler like cellulose nanocrystals have exceptional strength, a high aspect ratio, and easy surface functionalization and modification through their abundance of hydroxyl groups [134]. This makes them great rheology modifiers and mechanical reinforcers for many applications by having strong interactions with the polymer matrix and transferring stresses throughout the polymer. They are still organic, however, which makes them less suitable for applications requiring high heat ($> 300\text{ }^{\circ}\text{C}$) or extended exposure to heat [135]. Some other common fillers are calcium carbonate, silica, talc, and nanoclay [80,124,136]. Decreased chain mobility and increased crystallinity from filler addition will lower the final MFI of a polymer composite, as

the stronger and more ordered molecular interactions will make the composite more resistant to flow and changes in internal architecture [137].

2.2.3.2.3.2 Processing parameters

Outside of the intrinsic properties of the polymer melt, there are many other processing factors that impact the diameter of the melt-blown nonwoven fibers. The distance the collector is positioned from the die (DCD) has an impact on fiber attenuation rate, entanglement, cooling rate, and total cooling time [138]. Fibers produced at large DCDs are generally smaller in diameter due to the total time of attenuation from the high-velocity hot air. This also has an impact on the final nonwoven mat geometry and morphology, as increased chance of whipping and improved cooling rate at higher DCDs can vary the final mat thickness and porosity of the nonwoven mat [139].

Air temperature and pressure are also crucial parameters to consider when creating melt-blown nonwovens of a desired diameter. As one might expect, higher temperature air leads to lower diameter fibers, as the polymer experiences more of a melting effect from the air as they collide coming out of the die, further lowering its viscosity [140,141]. Increasing air pressure has also shown to decrease fiber diameter and impact the final geometry of the nonwovens. Higher air velocity/pressure will lead to greater fiber attenuation which decreases the fiber diameter [142]. However, if the air velocity overpowers the limited melt strength of the fine polymer fibers, this can lead to necking, fracturing, and the production of loose, unattached fibers. Therefore, lower air velocity systems are desirable both to limit fiber breakup and to save on production costs [138].

2.2.3.2.4 Porosity and pore size

For certain applications, such as filtration, the performance of melt-blown nonwovens is heavily dependent on the pore size and porosity of the fiber mat. Melt-blown nonwovens typically exhibit a porosity of around 70% - 99%, with the fabric fibers being anisotropic yet with some level of alignment [143]. As previously stated, processing parameters air pressure and temperature, fiber diameter, MFI, and DCD all impact nonwoven's pore size. Finer diameter fibers mean more open space in the fabric, which subsequently reduces pore size [144]. Post-processing calendaring and collector rotation speed will greatly impact the final porosity of the nonwoven fabric as thicker fabrics will decrease in porosity from the slow, continued stacking of layers on top of each other [145]. Work done by Kara and Molnar [138] showed that DCD initially decreased porosity up to 150 mm, and then caused it to increase after that. This is due to increased turbulence observed by the fibers at greater distances that causes them to diverge and spread out if given sufficient distance, ultimately reducing the packing density and creating a softer, airier nonwoven mat. Interestingly, increases in both air pressure and temperature both had an overall negative impact on the porosity and pore size of the nonwoven mats. High air pressures constricted the lateral movement of the fibers, leading to thicker and more densely packed nonwoven mats with smaller pore sizes.

Chapter 3: Styrene-ethylene-butylene-styrene (SEBS) melt-blown fibers for oil spill remediation and oil barrier geotextiles¹

3.1 Introduction

Accidental oil spills during storage, transportation, onshore and offshore exploration, and leakage from underwater pipelines represent one of the most severe environmental disasters with devastating consequences on various ecosystems, including aquatic flora and fauna, avian species, and terrestrial mammals, water supplies, as well as posing long-term chronic effects on human health and the ecosystems [146]. Strategies and technologies that hold the potential to mitigate the devastating impacts of onshore and offshore oil spills are necessary if such catastrophic events were to occur [147,148].

Oil spill remediation technologies can be broadly classified into physical, chemical, and biological categories [149]. Among the physical approaches, oil blooms and skimmers are extensively utilized for oil removal [150]. Chemical methods involve the application of dispersants, which are surfactants sprayed onto oil spills to break the interfacial tension, resulting in the formation of smaller oil droplets, facilitating easier dissolution and biodegradation [151]. Bio-stimulation and bioaugmentation represent two distinct approaches to bioremediation. Bio-stimulation involves introducing nutrients to encourage the proliferation of microorganisms, while bioaugmentation entails introducing additional microorganisms to the already existing native population that can naturally degrade the oil [146]. However, these methods have limited efficiencies and are not widely used in practical

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applications. This is mainly related to the remediation methods leading to secondary pollution and impose challenges on subsequent mitigation or oil extraction processes [152].

Thus, the design and application of appropriate remediation technologies are vital in devising effective and environmentally friendly oil spill response strategies [146]. The employment of absorbent materials has demonstrated superior effectiveness and economic viability compared to other methods [152,153]. These materials are often oleophilic and hydrophobic, enabling efficient oil removal. Materials investigated for such application include natural biomass (e.g., peat, hay, ground corncob), inorganic materials (e.g., perlite, vermiculite, clay, wool), or synthetic (e.g., polyethylene, nylon fibers) [154,155]. Absorptive polymers, pioneered by Richard Hall [156] at Dow Chemical's Central Research Department, have been used to effectively absorb organic solvents, oils, chlorinated, and aromatic solvents. The oil absorbency of these materials is influenced by the degree of crosslinking and hydrophobicity of the polymer structural units [156]. While polyurethane sponges have been employed for oil-water separation, their poor selectivity in conjunction with low mechanical durability in harsh conditions remains a challenge [157]. Other polymer foams with an open cell structure (e.g., polypropylene, polystyrene) are also used as synthetic organic absorbents in oil spill cleaning applications.

Recent studies suggest that non-woven fibers are optimal for oil adsorbents due to increased surface area, rapid adsorption, and potential for future development [158]. The suitability of a sorbent for oil spill applications depends on factors such as oil retention, void fraction, wettability, and physical configuration of the fibers [159,160]. For instance, melt-

blown nonwoven fibers of polypropylene (PP) find commercial usage as adsorbent materials, where they can be structured into webs, fabrics, sheets, and pads [158,159]. Classical PP fibers take in oil through two mechanisms: adsorbing oil on the fiber surface via van der Waals forces and capillary action by sipping oil between fiber voids without interacting or penetrating the material's internal structure [158]. Due to its high specific surface area (fine fiber diameters) and lipophilicity, PP exhibits enhanced oil adsorption during the initial sorption kinetics [161].

However, a drawback of adsorption of oil is that when the material reaches saturation, it can no longer adsorb additional oil, potentially causing oil dispersion or leakage. Additional physical contact or osmotic pressure by solvents, or water may leach the adsorbed oil. Consequently, there is a significant demand for alternative materials that exhibit enhanced interactions with the sorbent, enabling efficient oil capture and effective sealing to prevent leakage [162].

SEBS thermoplastic elastomers are triblock copolymers derived from the hydrogenation of styrene-butadiene-styrene (SBS) with highly ordered polystyrene domains serving as the hard blocks, and a flexible region formed by the ethylene-butylene soft block held together by the hard blocks [163]. The unique chemical structure of SEBS elastomer not only grant the polymer remarkable strength, elasticity, and flexibility, but also gives it plastic-like processability through industrial processes, such as injection molding, extrusion, and melt-spinning [162,164]. More importantly, SEBS can capture oil through a unique gelation mechanism, wherein the rubbery ethylene-butylene midblock dissolves in oil while the glassy styrene end blocks do not, allowing the polymer to capture the oil without

complete dissolution. Consequently, it has emerged as a promising material for oil spill remediation and oil spill mitigation geotextiles.

The gelation of SEBS, driven by non-covalent interactions like van der Waals forces, pi-pi stacking, and hydrogen bonding, facilitates efficient oil removal without dispersing the oil further in the water. Moreover, the gelation generates a barrier preventing further oil/hydrocarbon spreading despite saturation with oil/hydrocarbons [157,162]. The melt-blowing of SEBS can be perceived as an interesting method to capitalize on this gelation mechanism, due to the increased surface area provided by the thin fibers for better absorption kinetics [161,165]. However, the melt-blowing of thermoplastic elastomers, including SEBS, is challenging attributed to the high viscosity or low melt flow index (MFI) of such polymers, because of their large molecular weight and the styrene block that limits its flow. Thus far, limited research has been conducted to produce a functional melt-blowing system comprising only pure SEBS. Thus, optimal processing temperature that enhances the flow properties of SEBS while avoiding thermo-degradation need to be established for the melt-blowing of thermoplastic elastomers, including SEBS.

This study explores the fabrication of melt-blown SEBS non-woven with a high specific surface area and their application as an effective oil sorbent material by taking advantages of the distinctive oil/hydrocarbon gelation properties of SEBS, as well as the enhanced porosity and highly increased surface area obtained from the melt-blowing process technology. While there is limited research on the successful melt-blowing of SEBS [166,167], most studies incorporate blending additives to mitigate the low melt-flow capabilities of SEBS. Previous

work by Lee et al. [168] explored how the blending of SEBS and low molecular weight poly(propylene) (PP) could increase the melt flow index (MFI) and improve the processability of the melt-blown nonwovens. However, due to the substantial viscosity variation between the SEBS and PP, the blend compatibility was rather underwhelming. While the resulting nonwovens composed of 80 wt% SEBS and 20 wt% PP provided efficient oil ab/adsorption performance, the processing was energy intensive, the fiber dimension was variable with poor dispersion of PP in the SEBS matrix that caused.

Thus, it was imperative to investigate processing of pure SEBS into melt blown fibers and evaluate their oil ab/adsorption and gelation properties for oil spill mitigation. For this, low viscosity (high MFI) SEBS was selected, and the rheology was characterized using rotational and capillary rheometers. The melt blowing process was then developed using a mini-twin screw extruder. Consequently, the oil sorption capacity and gelling kinetics of melt-blown nonwovens were analyzed for selected types of oil, including mineral-based transformer oil, vegetable-based transformer oil, gasoline, diesel, and crude oil. The practical applications of the fabricated material for oil/hydrocarbon spill mitigation and oil/water separation were also highlighted based on a series of rational experiments in order to indicate the performance capabilities of the nonwoven materials. The obtained results were compared with the performance of nonwoven PP fibers.

3.2 Materials and methods

3.2.1 Materials

Polypropylene (PP) in pellets form (average molecular weight of 72,500 g/mol) was acquired from LyondellBasell Industries (Texas, USA). Styrene-ethylene-butylene-styrene (SEBS) (styrene/rubber ratio 13/87, Brookfield viscosity 4200 cps at 25 °C was provided by Kraton corporation (Texas, USA). Hyvolt (mineral transformer oil) was purchased from Ergon Specialty Oils (MS, USA), FR3 natural ester dielectric fluid (vegetable transformer oil) was obtained from Cargill (MN, USA), gasoline oil and diesel oil were purchased from Esso (ON, Canada), and crude petroleum oil was obtained from Pembina (AL, Canada). Oil soluble dyes (Oil Blue N) were obtained from Sigma-Aldrich (MO, USA). All materials were used without further modification or purification.

3.2.2 Methods

3.2.2.1 Meltblowing

A horizontal twin-screw extruder (Process 11 Parallel Twin-Screw Extruder, Thermofisher Inc) equipped with a customized melt-blow die was used to produce non-woven mats. The custom-made melt blowing nozzle is illustrated in **Figure 3.1a**. The gas flow direction and the custom-made die bore a resemblance with Exxon slot dies, frequently employed in commercial melt-blowing processes [169–171]. The external angled cap was comprised of five outer hole diameters measuring 2.5 mm each, featuring a converging air jet (at an angle of 128°). This cap was coupled with heated nitrogen gas, facilitating the stretching and heating necessary for producing fine and distinct melt-blown fibers. The incoming nitrogen gas was linked to a

750 W heater (set to 350 °C) and connected to blowing die. The heater temperature was controlled by a transformer (Powerstat® Variable Transformer, Superior Electric Co, Ohio, USA). The polymer (SEBS/PP) powder was fed (3.5 g/min) into the twin screw extruder and processed with a temperature profile of 240/260/280/300/300/300/300/300/300 °C, at 150 rpm screw speed, and collected at a die-to-collector distance (DCD) of 40 cm (based on preliminary optimization work).

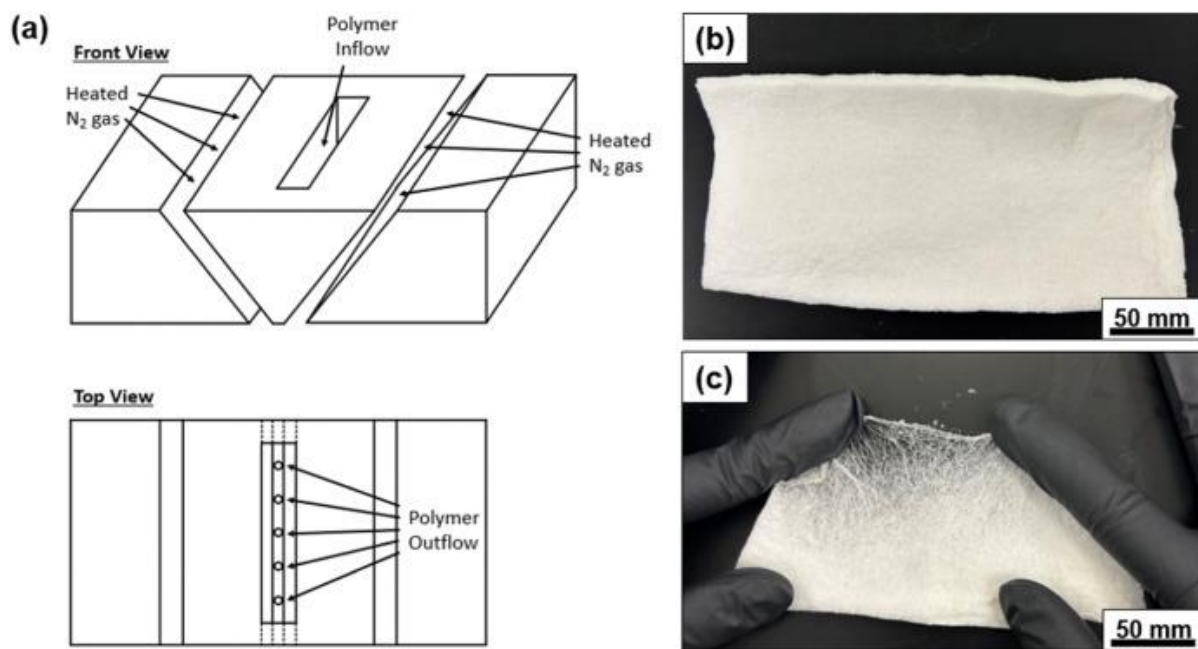


Figure 3.1. (a) Assembly of the melt-blown die set-up, (b) SEBS fiber mat produced by melt blowing, and (c) Stretched SEBS fiber in the mat.

The volumetric flow rate of the nitrogen gas used for the melt-blowing process was set-up at 0.5 L/min (based on preliminary experimentation) to provide sufficient heated air pressure to stretch the SEBS fibers. The fiber collector had a DCD and rotational speed of 40 cm and 60 rpm, respectively, to ensure proper fiber solidification before collision. An aluminum based

slow rotating (30 rpm) drum was used to collect the non-woven mat after the melt-blowing. Fiber solidification was further aided by the employment of a mechanical air-cooling gun placed close to the collector. The fibers were then collected as fiber mat, which was displayed in **Figure 3.1 (b & c)**.

3.2.2.2 Capillary rheology

To assess the polymer rheology under the melt-blowing operating parameters, the melt rheology characteristics of SEBS and PP were evaluated using a capillary rheometer equipped with dual bore piston (Rosand Advanced RH2000, NETZSCH Group, Germany). Prior to the rheology measurement, the rheology specimens were dried (120 °C, 2h) in a convection oven. The rheology analysis was then conducted (300 °C) in the shear rate range of 20 to 10,000 s⁻¹. In one bore, the capillary had an L/D ratio of 16/1 and a diameter of 1 mm, while the orifice die in the other bore was a nearly zero-length capillary. During the measurement, Rabinowitch and standard Bagley corrections were implemented to consider the pressure drop effect of the molten SEBS/PP polymers as they entered the capillary.

3.2.2.3 Melt flow index (MFI)

The ease of flow of the melt of the SEBS elastomer and PP thermoplastic polymer were assessed with a melt flow indexer (LMI 4000 series, Dynisco, Massachusetts, USA). The MFI tests were performed in accordance with ASTM D1238 method and by employing a load (2.16 kg) at temperatures of 230 °C and 300 °C.

3.2.2.4 Fiber characterization

The non-woven fibers were analyzed via a polarized optical microscope (POM) (Olympus BX53 M microscope, Olympus Corporation, Tokyo, Japan). For this, the non-woven SEBS and PP fiber samples were placed between two glass slides and pictures were collected at 10x magnification. The dimensions of the fibers were estimated using a built-in measuring tool in the Olympus Stream Basic software. The diameter distribution of the fibers was determined from the measured average of approximately 150 fiber diameters for both SEBS and PP fibers. Additionally, a field emission scanning electron microscopy (FESEM) (FEI Quanta Feg 250, Oxford Instrument) was employed (voltage of 20 kV, 100x magnification) to analyze the dimensions and morphology of the fibers. A sessile drop technique was employed to determine the water contact angle (WCA) and the selected oil contact angle (OCA) of both SEBS and PP fibers. Each fiber mat was subjected to a 5 μ L droplet of deionized water and selected oils, and images of the droplets were captured after 0.2 s of dispensing the liquids. The 0.2 s interval was chosen to prevent the water from diffusing into the non-woven mats before the measurement. An image processing software (ImageJ) was then used to estimate the contact angle.

The mechanical properties, including tensile strength, tensile modulus, and elongation at break, were evaluated using a Universal Testing Machine (UTM, AGS-X series, Shimadzu, Japan). The specimens, with predetermined dimensions, were subjected to the testing. The testing was performed in tensile mode at room temperature, using a 500 N load cell, and

a strain rate of 500 mm/min and 100 mm/min for SEBS and PP, respectively. The reported results present the mean and standard deviation of at least 5 tested specimens.

3.2.2.5 Parallel plate rheology

To understand the gelation of the fibers in contact with oils, rheological characterizations was carried out using a HAAKE MARS III Rheometer equipped with parallel plate geometry (1 cm diameter disc at 3 mm gap width). Initially, the linear viscoelastic region (LVR) was established and 1% strain was selected for an oscillatory frequency sweep test. Subsequently, the frequency ramp tests (100–0.01 Hz) were carried out at room temperature (25 °C). To assess gelation, the SEBS non-woven specimens were placed on the rheometer disk plate, and oil (various types) was directly applied to the mat surface at three different mass ratios, which were 1:1 (fiber mat: oil), 1:2.5 (fiber mat: oil), and 1:5 (fiber mat: oil). Following this, a frequency sweep test was conducted to analyze the variation in the rheological parameters during the gel formation. The results were then compared to those obtained from PP fiber mat samples, which did not exhibit gel formation when interacting with the oil samples. This distinction is evident from the critical viscosity, storage modulus, and loss modulus graphs.

3.2.2.6 Oil sorption

3.2.2.6.1 Maximum absorption

The oil absorption capacities of the fibers were tested in five types of oils, i.e., Hyvolt oil, FR3 oil, crude oil, gasoline, and diesel. 1 cm × 1 cm pieces of SEBS and PP melt blown fibers were prepared and accurately weighed. Following the fiber-to-oil ratio of 1:10, an appropriate

amount of oil for each piece was measured. For the SEBS fibers, the samples were placed in a cup and oil, calculated according to the fiber to oil ratio of 1:10, was poured onto it. After 15 s, the amount of oil absorbed by the SEBS fiber was examined. This procedure was then repeated for all five types of oils. Triplicate of each sample were taken to determine the average of the results.

The oil sorption capacity Is demonstrated in the following Equation (3.1):

$$\text{Oil Sorption (\%)} = \frac{W_1 - W_0}{W_0} \times 100 \quad (3.1)$$

where W_0 is the weight of the original fiber mat specimen and W_1 is the mat weight after oil sorption.

To observe the gelation process, the cups were left overnight, extra oil was removed, and subsequently the amount of resulting semi-solid gel was weighed.

The gel formation capacity was then calculated based on equation (3.2):

$$\text{Gel Formation Capacity (\%)} = \frac{W_2 - W_0}{W_0} \times 100 \quad (3.2)$$

where W_0 is the weight of the original fiber sample and W_2 is the weight of the solid fiber/oil gel.

The same experiment for oil absorption and gelation was then repeated for PP fibers for comparison purposes.

3.2.2.6.2 Oil water selectivity

The application of oil absorption selectivity of SEBS fibers was demonstrated by the immersion of the SEBS fibers in oil-contaminated water. 5 mL of Hyvolt, FR3, and Crude oil were added into separate beakers filled with 70 ml of water. SEBS fibers were prepared in squares of 1×1 cm and individually immersed in the beakers to examine the performance of oil absorption of the fibers while leaving the water. The experiment was repeated for PP fibers to provide a reference for oil cleaning performance comparison.

3.2.2.7 Oil water separation

The oil-water separation test was conducted using a customized home-made setup, as illustrated in **Figure 3.9**, **Figure 3.10**, which comprised of a graduated cylinder, a small graduated-cylinder open from both sides, a weight, and a funnel. A 15 cm diameter circular fiber mat was prepared and positioned between both cylinders in such a way that it remained securely in place. To ensure stability, a weight was applied to compress the fiber from the sides, preventing any movement or leakage. A 100 mL mixture with 3:7 oil-to-water volume ratio was poured into the setup for each of the three oils- Hyvolt, FR3 and Crude oil.

3.3 Results and discussion

3.3.1 Rheology and melt flow analysis

The production of melt-blown nonwovens involves processing the molten polymers through multiple small capillary nozzles, where the polymers then in contact with the high velocity heated gas (N_2) so that the fibers could be stretched out into microfibers. Thus, capillary rheology analysis can give an excellent indication of the performance of a given compound

under these conditions as the test evaluates the flow of polymers through a cylindrical channel over a range of shear rates. The corrected shear viscosity and corrected shear stress were evaluated as functions of corrected shear rate for both thermoplastic materials and results are shown in **Figure 3.2(a-b)**. Both SEBS and PP show clear shear thinning (pseudoplastic) behaviour which is common amongst thermoplastics. This behaviour is characterized by a linear decrease in shear viscosity with increasing shear rate. This linear trend over the complete range of processing shear rates is in accordance with the classic power law relationship, as seen in equation (3.3), where η corresponds to shear viscosity and $\dot{\gamma}$ corresponds to shear rate.

$$\eta = K\dot{\gamma}^{n-1} \quad (3.3)$$

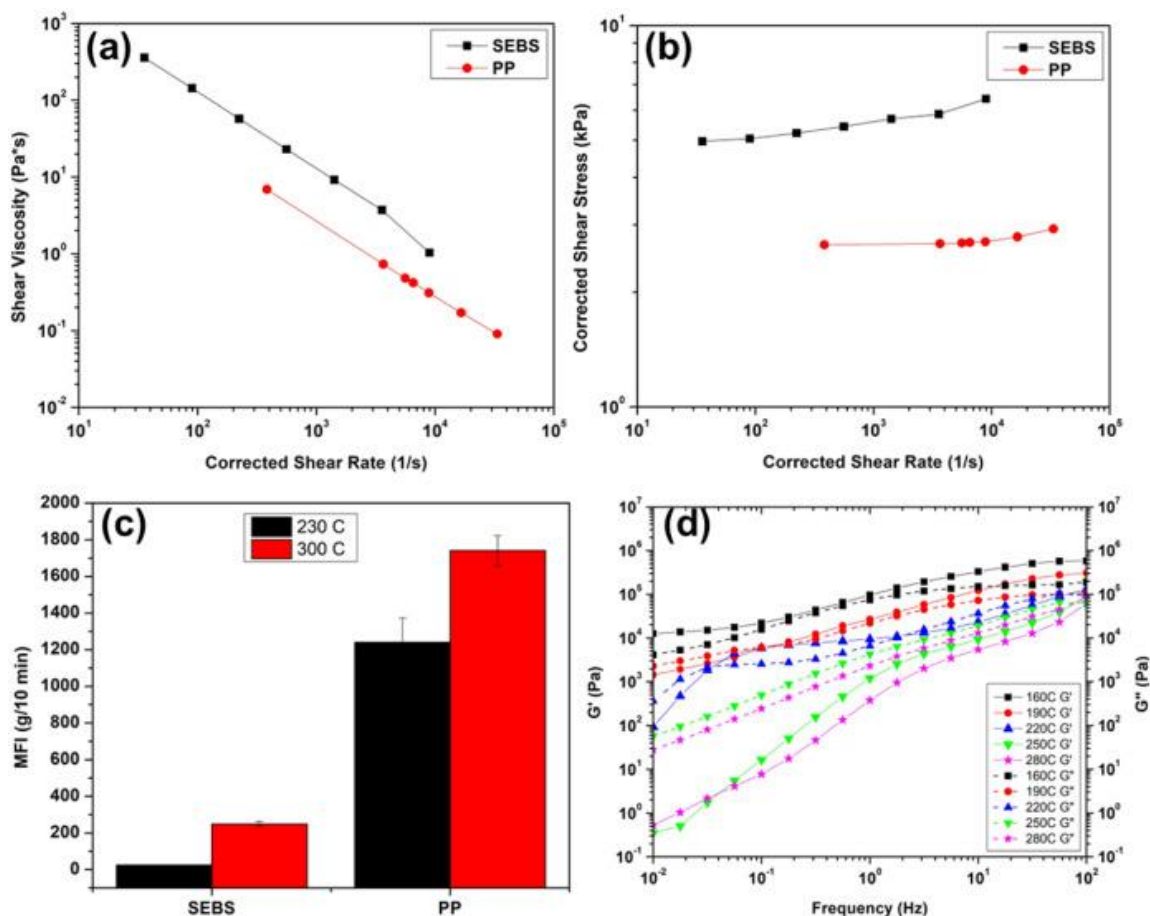


Figure 3.2. Capillary rheology curves demonstrating (a) shear viscosity and (b) shear stress of SEBS and PP versus shear rate at 300 °C; (c) Melt flow index of SEBS and PP resins; (d) Melt rheology of SEBS from 160 to 280 °C.

As expected, the selected PP grade displayed low viscosity, which makes it preferable for melt blowing processes as finer diameter of fibers can be produced from the melted polymers. On the other hand, the shear viscosity of SEBS was observed to be much higher, indicating that the thermoplastic elastomer SEBS's flow through the nozzle could not be as smooth as PP's flow nor the fibers would be as fine as the PP's. Nevertheless, the flow behaviour of SEBS at 300 °C as measured by capillary rheometer still display low range of shear viscosity, showing

that the processing temperature is sufficient for melt-blowing processes. MFI was also conducted to further evaluate the efficiency of different processing temperatures, as depicted in **Figure 3.2(c)**. Both PP and SEBS exhibited a significantly higher melt flow index at high temperature (300 °C) as compared to its performance at lower temperatures (230 °C). The SEBS exhibited an 872% increase in mass flow, from 25.7 to 249.9 g/10 min, corresponding to the temperature increase from 230 °C to 300 °C. Meanwhile, the MFI of PP increased by 40% in material mass flow, from 1240.8 to 1740.2 g/10 min over the same increase in temperature.

The viscoelasticity and melt-flow behaviour of SEBS was further examined with parallel plate rheology over a wide temperature range of 160–280 °C (**Figure 3.2(d)**). The parallel plate rheology analysis showed that 280 °C and above is required for SEBS to display a truly viscoelastic fluidic behaviour, with G'' greater than G' , over the full frequency range. In contrast, even at 250 °C, there is at least a small portion at high frequency where SEBS is still dominated by elastic flow. These tests in conjunction with capillary rheology and MFI demonstrate the need to process SEBS at high temperatures (>280 °C) to achieve sufficient fluidity required to generate melt-blown nonwoven fibers. Rotational rheology evaluation close to 300 °C was not carried out in this study due to the limitation of the equipment.

3.3.2 Fiber characterization

The morphology and dimensions of the nonwoven fibers was evaluated by employing SEM (**Figure 3.3(a-d)**). Microscopy observations revealed that both non-woven fabrics have fiber diameters in the micron range (1–70 μm). The PP fabric produced was fluffier, owing to its

smoother plastic-like surface and ductility, and exhibited a porosity of 95%, as defined in equation (3.4):

$$\phi = 100 - \left(\frac{m}{\mu \times V} \times 100 \right) \quad (3.4)$$

where ϕ is the porosity, m is the mass of the mat (g), μ is the density of the polymer (g/cm³), and V is the total volume of the mat (cm³).

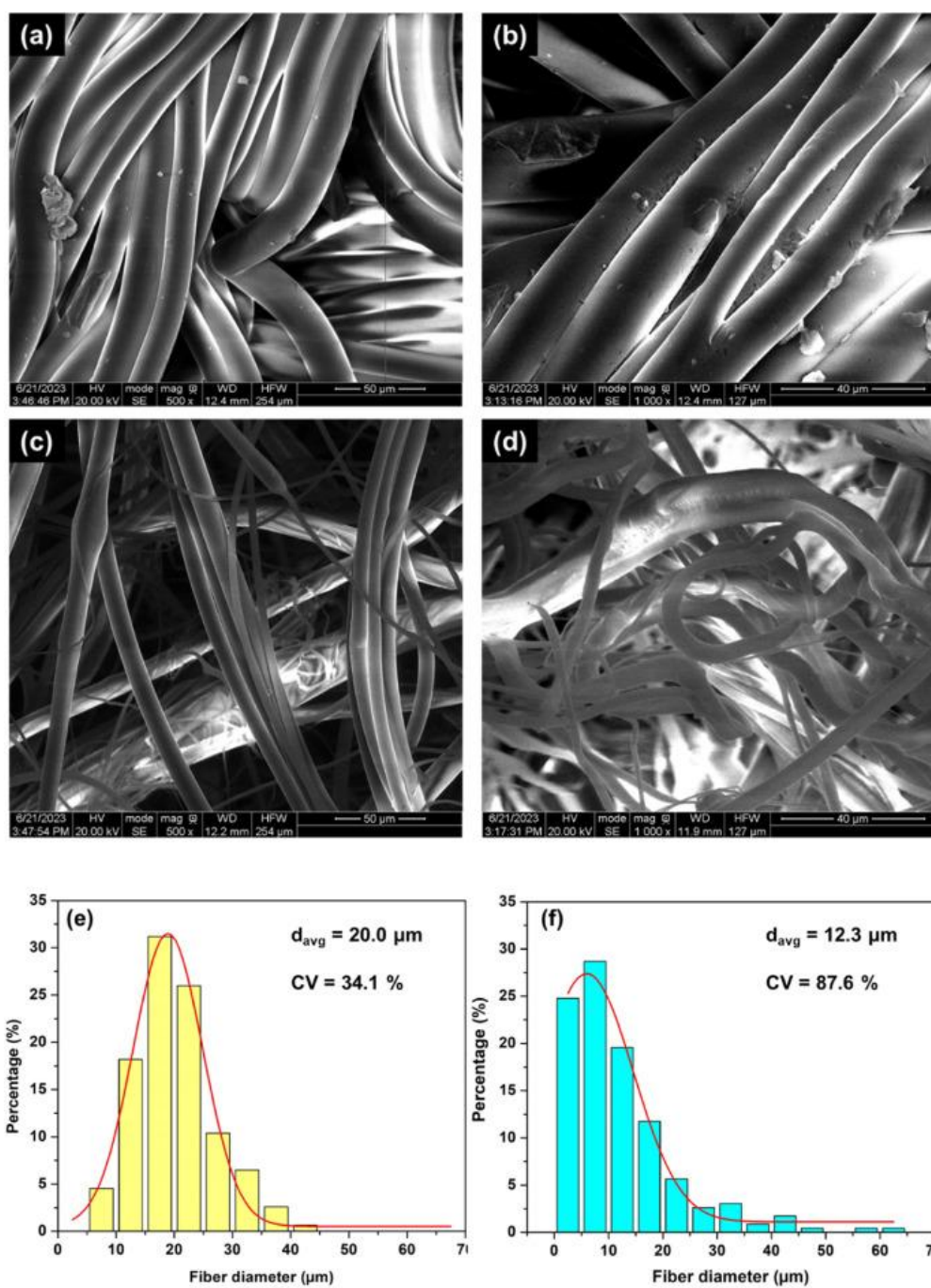


Figure 3.3. SEM images of nonwoven fabrics of SEBS fibers at (a) 500x and (b) 1000x magnification, nonwoven fabrics of PP fibers at (c) 500x and (d) 1000x magnification; fiber diameter distribution for SEBS (e) and PP (f).

Fiber diameter can greatly affect the initial oil adsorption process since smaller fiber diameter directly correlated with higher surface area exposure of the melt blown nonwovens to the oils. This can in turn help accelerate the rate of ad/absorption and therefore gelation. The PP fabric has an average fiber diameter of 12.3 μm , as seen in **Figure 3.3(f)**. On the other hand, the SEBS fibers produced had average diameters of 20.0 μm and, are inherently more elastomeric, were more tightly packed together with a porosity of 85%, as seen in **Figure 3.3(e)**. Overall, it appears that the PP fibers diameter was only slightly significantly lower than those of SEBS. Due to small diameter sizes, both pure SEBS blend and PP fibers are expected to possess rapid rates of oil absorption due to increased surface area of oil exposure. It was also noted that the SEBS fibers provided enhanced uniformity, as noted from the low coefficient of variation (CV) (34.1 %). On the other hand, the microscopy observations revealed many frizzy and entangled PP fibers with various and inconsistent fiber diameter sizes, which was reflected from the high CV (87.6 %) showing a broader diameter range. Some extremely small PP fibers were also observed on the microscopy images, which can be referred to as “flies.” These “flies” can be attributed to breakup of the PP fibers while processing, which could be caused by excessive temperature or pressure while processing [172]. So, while the extreme processing conditions of 300 °C extruder temperature was necessary to produce SEBS melt-blown fibers, the selected temperature may be too extreme for processing traditional PP fibers, which could have resulted in the PP fibers breakup.

The mechanical properties of the non-woven fabrics were investigated via tensile testing, and the results are displayed in **Figure 3.4(a – d)**. As anticipated, the non-woven fabric

possesses low tensile strength, which were 0.10 and 0.15 MPa for PP and SEBS, respectively, attributed to lack of chemical bonding or major entanglements amongst the fibers. The slightly higher tensile strength of the SEBS fabric could be contributed to the inherent tensile property of the higher molecular weight SEBS as compared to the low molecular weight PP, as deduced from the rheology and MFI investigations. Additionally, the larger diameter of the SEBS fibers in the nonwoven mat as compared to the PP fibers could correlate with the observed higher tensile strength. SEBS, being a thermoplastic elastomer (TPE), has a significantly higher elongation at break at 1678% compared to the more brittle PP fabric with 125%. As expected, the elastic modulus of the SEBS was lower compared to PP, which was also attributed to the elastomeric nature of the SEBS TPE compared to PP thermoplastic.

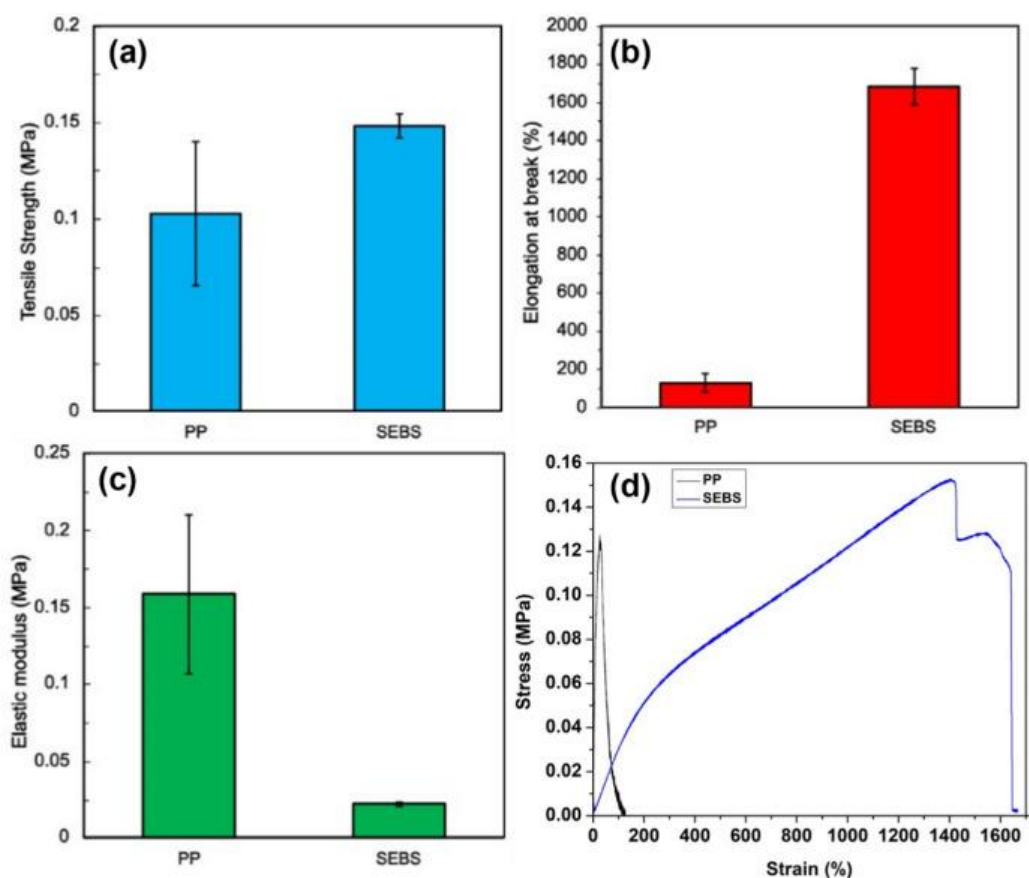


Figure 3.4. Tensile properties of PP and SEBS nonwovens showing (a) tensile strength, (b) elongation at break, (c) elastic modulus, and (d) Typical stress-strain curve of PP and SEBS.

3.3.3 Oil and water interaction

3.3.3.1 Water contact angle and oil contact angle

The main application target of the non-woven mat made from SEBS was for oil spill mitigation and oil – water separation. Thus, in order to gain a comprehensive understanding of the SEBS fabric's interaction with water and oil, tests were conducted for SEBS and PP fibers with five different oils: mineral-based transformer oil (Hyvolt), vegetable-based transformer oil (FR3),

gasoline, diesel fuel, and crude oil to examine the interaction of the fiber mats with different type of oils.

The hydrophobicity/lipophilicity of the nonwovens can be evaluated via water contact angle (WCA) and oil contact angle (OCA) tests. Due to the porous nature of the fabrics, instantaneous contact angle measurements were essential to ensuring accurate results. The hydrophobic nature of SEBS was found to be very comparable to that of PP, as seen in **Figure 3.5**, which has a well documented history of being hydrophobic and capable of adsorbing various types of oil [173–175], and any differences between the two were statistically insignificant. The oil contact angle showed low contact angle ($CA < 60^\circ$), which were observed for the Hyvolt, FR3, and crude oil, indicating that both SEBS and PP have great affinity with the oils. However, no comparison could be conducted with gasoline or diesel oil as the SEBS fibers dissolved too quickly in the oil to capture a photo, which was less than 0.1s dissolution time. This is most likely due to the benzene content present in automotive fuel dissolving the glassy styrene blocks of the SEBS that are responsible for the gelling phenomenon of SEBS [176,177].

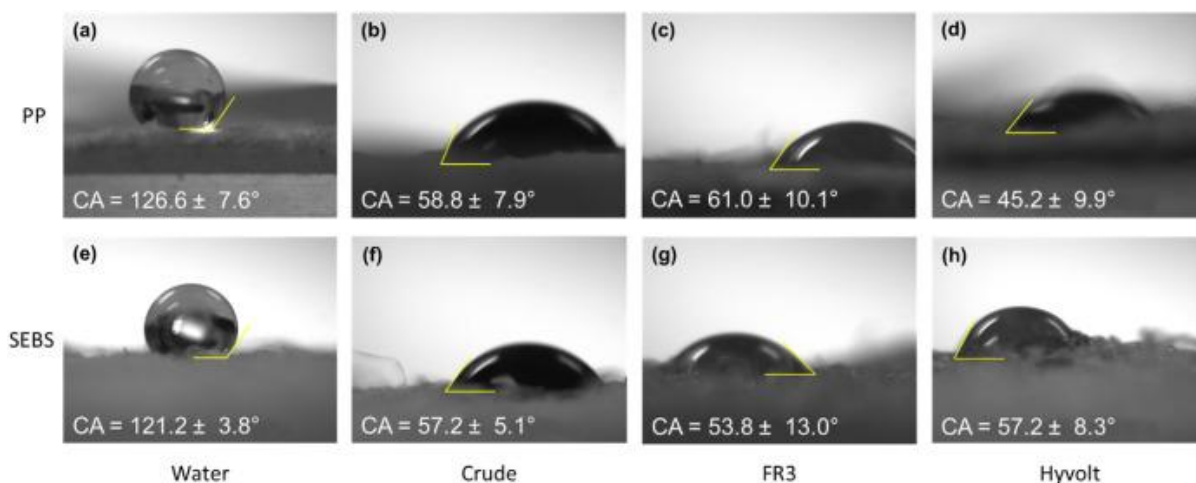


Figure 3.5. Water contact angle (WCA) of (a) PP and (e) SEBS; oil contact angle (OCA)(b–d) PP and (f–h) SEBS.

3.3.3.2 Gelation mechanism of SEBS with oil

Further investigation of the gelling mechanism of SEBS when in contact with each respective oil was conducted through the gelation study using parallel plate rheology (**Figure 3.6**). Various concentration of oil was applied directly to the surface of the nonwoven fibers to produce SEBS gels. The selected fiber mass/oil ratios were 1:1, 1:2.5, and 1:5 times, respectively. The rheological assessment was then conducted to evaluate the flow behaviour of the gels. The transition from a solid fabric to a viscous gel is seen when the loss modulus crosses over the storage modulus as the frequency moves from high (100 Hz) to low (0.01 Hz). The parallel plate rheology analysis of SEBS in **Figure 3.6** showed the effect of utilizing the nonwoven fabric for the absorption of different oils. At 1:1 ratio of the fabric to oil, no gelation was observed, which was most likely attributed to the capillary forces being insufficient for the sorption of the oil at smaller quantities. This amount of oil was also likely

insufficient to interact with all the SEBS present, meaning that even with small amounts of gelation present, it would not affect the overall rheological profile of the sample. When the oil amount was increased to a 1:2.5 mass/oil ratio, the samples containing Hyvolt and crude oil had visible gels on the outside, however the oil amount was still insufficient to cause detectable gelation with rheological analysis. This gelation did become apparent when a 1:5 (mat to oil) was used. However, the FR3 oil, which has poor interaction with the SEBS fibers, was still held within the fabric through traditional sorption mechanics and did not show any signs of gelation even with the 1:5 ratio. On the contrary, gasoline and diesel presented an intriguing rheological behaviour where the sample started out in a soft liquid-like gelling state and transitioned to a solid gelling behaviour by the end of the test. This observation can be attributed to the immediate dissolution of the fabric by the oil, as was seen during OCA analysis. As the test progressed, the dissolved portion of the sample flows away, leaving the protected solid portion of the sample with poor gelation mechanics to then become dominant, pushing it back towards the solid region. This behaviour, in conjunction with the OCA testing led to gasoline and diesel being omitted from all future tests as SEBS has proven to be an ineffective for the capture of these oils. **Figure 3.7** shows the behaviour of the PP fabric tested under the same conditions. All tests showed no generation of a gel as was expected, which were all reflected on the rheological analysis where the G' and G'' did not exhibit any crossover point indicating that the fiber remains in the viscoelastic solid state. This demonstrates that the PP mats rely exclusively on adsorption and capillary forces for the containment of oil, with interaction only happening on the surface of the fibers. Meanwhile, SEBS possess both adsorption and absorption capabilities toward the oil, which helps SEBS take in all the oil and

gel to contain the oil. The viscosity of all ten samples (not shown) shows a consistent decreasing trend as more oil is added to the sample, as the oil acts as a lubricant between the fibers and decreases the resistance between them.

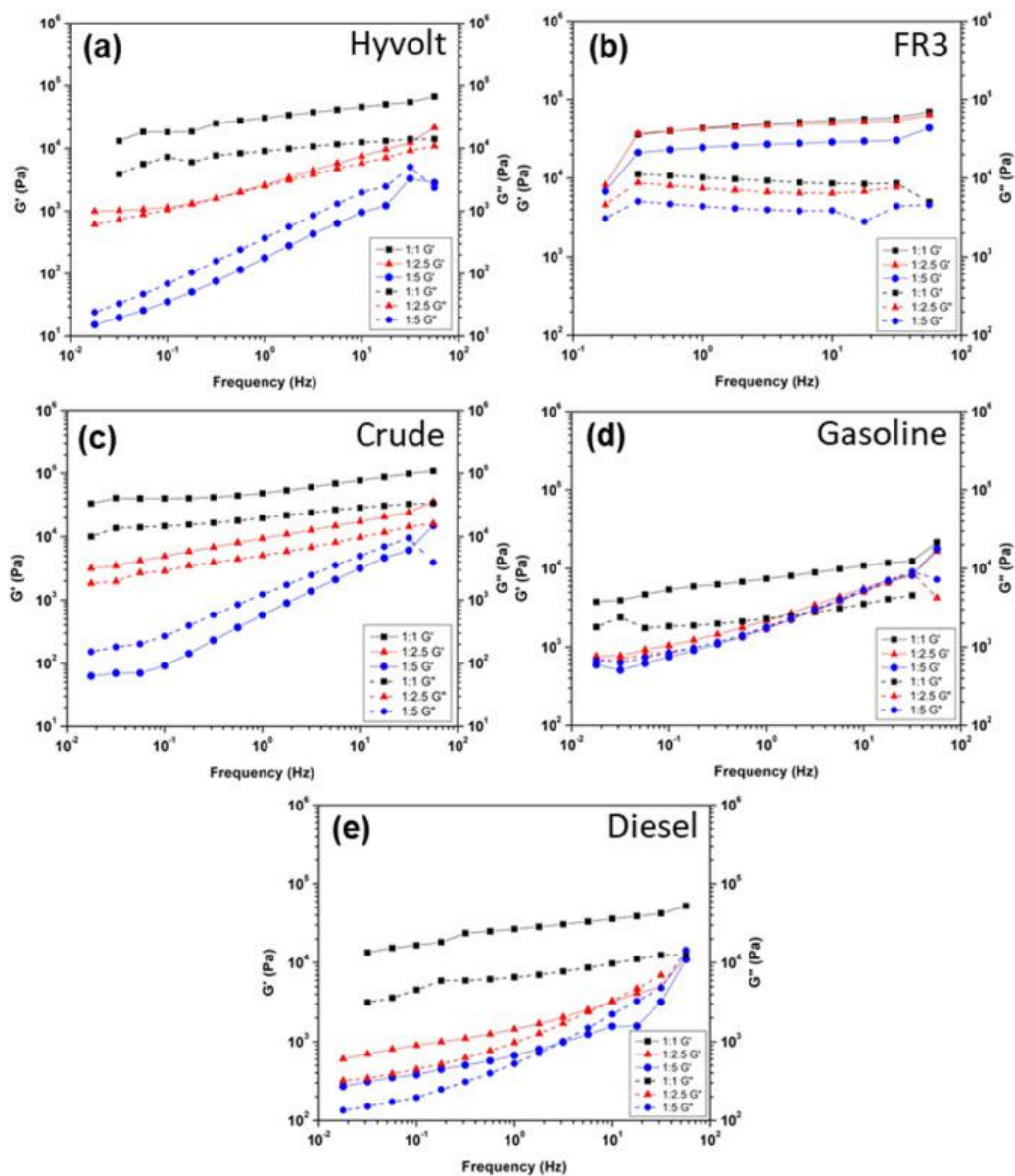


Figure 3.6. Gelation rheology of SEBS nonwovens with each corresponding oil.

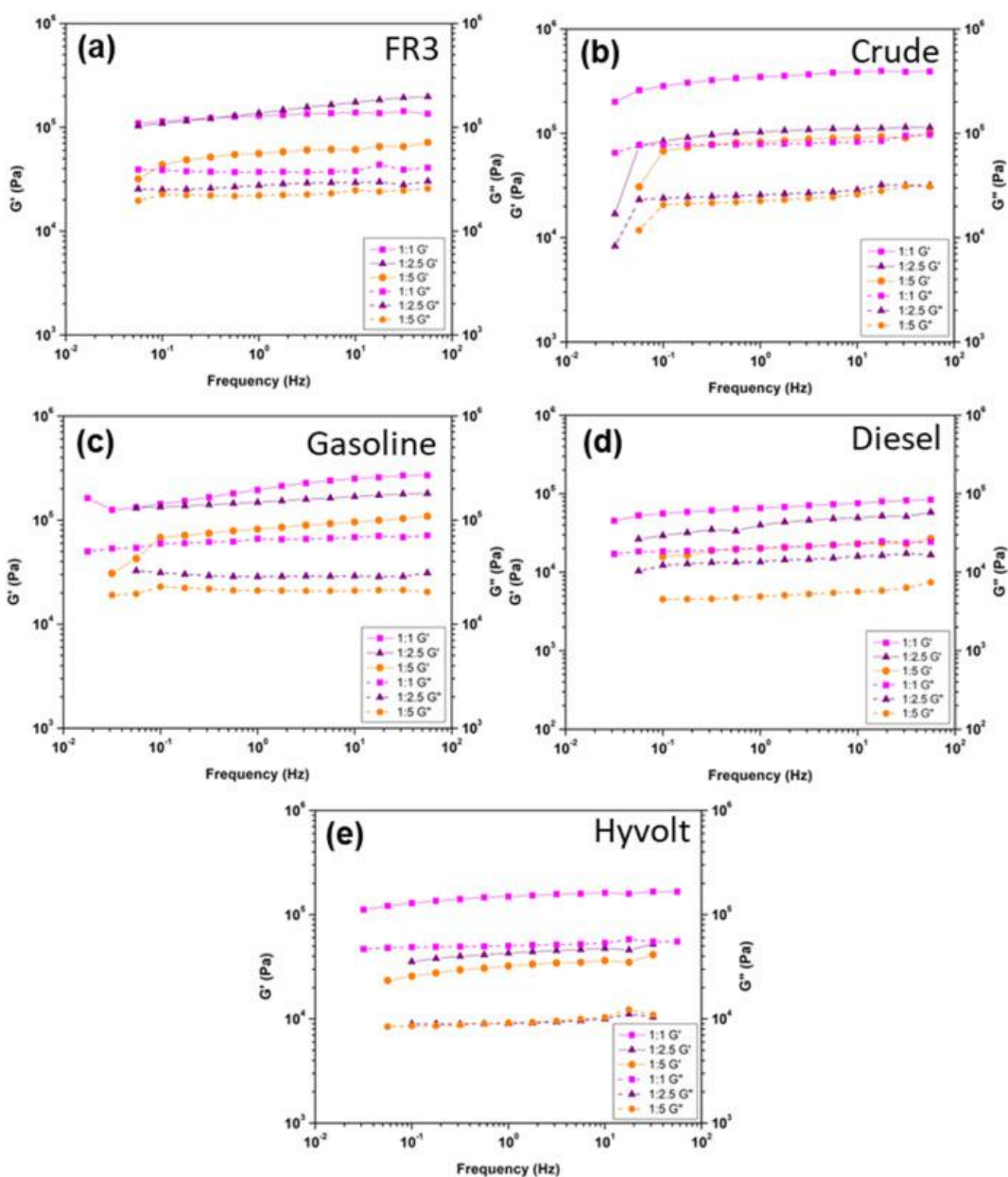


Figure 3.7. Gelation rheology of PP Nonwovens with each corresponding oil.

3.3.3.3 Gel formation capacity and oil/water separation application

In order to evaluate the level of interaction between each oil and the mats, immediate oil sorption testing was conducted, as seen in **Figure 3.8(a)**. The mats were exposed to a 1:10

(fiber: oil) mass ratio for 30 s to give ample time for the oil to permeate into the fibrous network. It was observed that all samples held their shape after 30 s, indicating that the dominant sorption kinetics were capillary forces and surface adsorption as opposed to material gelation. SEBS fibers, being elastomeric in nature, stretched to allow for the fabric to swell in size, increasing the maximum amount of oil capable of being captured. Moreover, Hyvolt oil once again demonstrated a higher level of affinity to the SEBS than other oils with 484 wt% oil being captured initially by the fabric. Crude oil and FR3 oil were sorbed at 439 w% and 426 wt %, respectively, although the differences was statistically insignificant. The result indicates high absorption capabilities of SEBS fiber. The adsorption of PP was observed to be initially higher than that of SEBS, due to the smaller diameter fibers and higher porosity. The PP fabrics were able to retain nearly twice as much oil as the SEBS fabrics on average. The only oil showing statistical difference when adsorbed by PP was gasoline. This may simply be the result of the higher content of volatiles in gasoline, meaning that the amount of gasoline present in the sample at the end of the 30 s is different to what was there at the beginning due to evaporation of components of the gasoline.

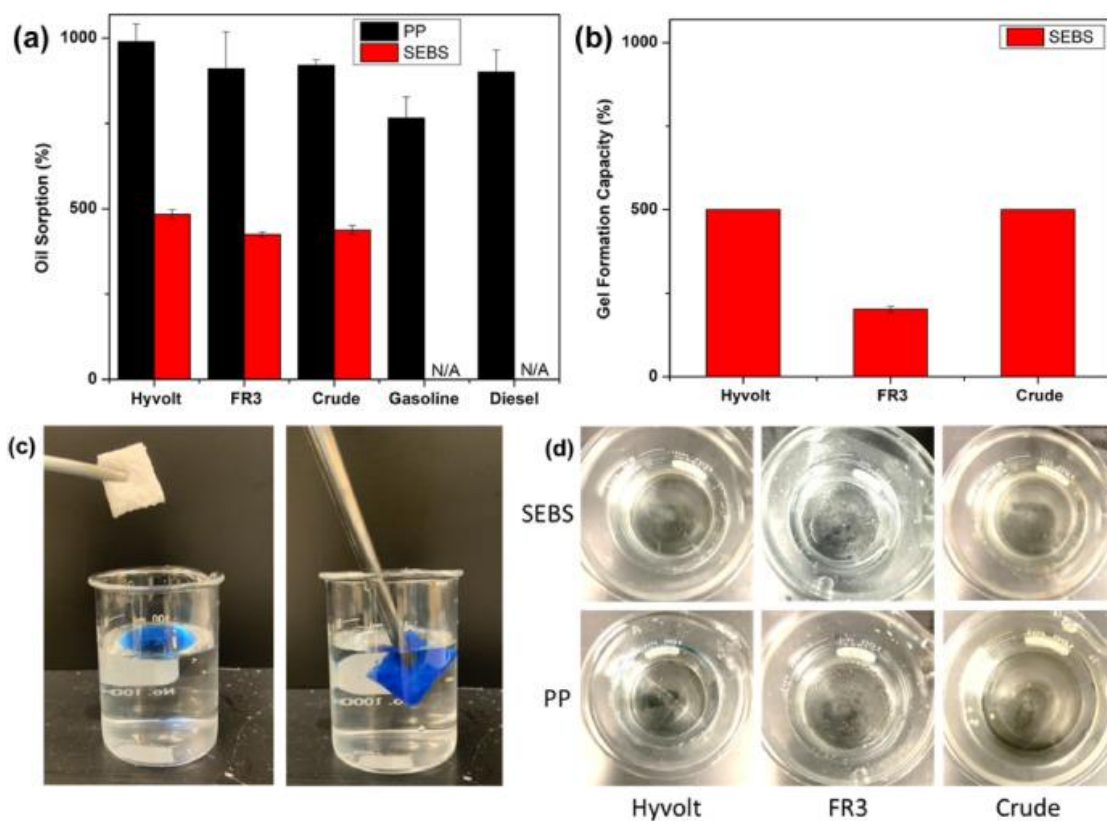


Figure 3.8. Oil sorption (a) of SEBS and PP nonwovens; (b) Gel formation capacity of SEBS fibers (standard deviation for Hyvolt and crude oil are negligible from triplicate measurements); (c) Blue-dyed Hyvolt oil gets absorbed in the immersion test; (d) Water quality after immersion test.

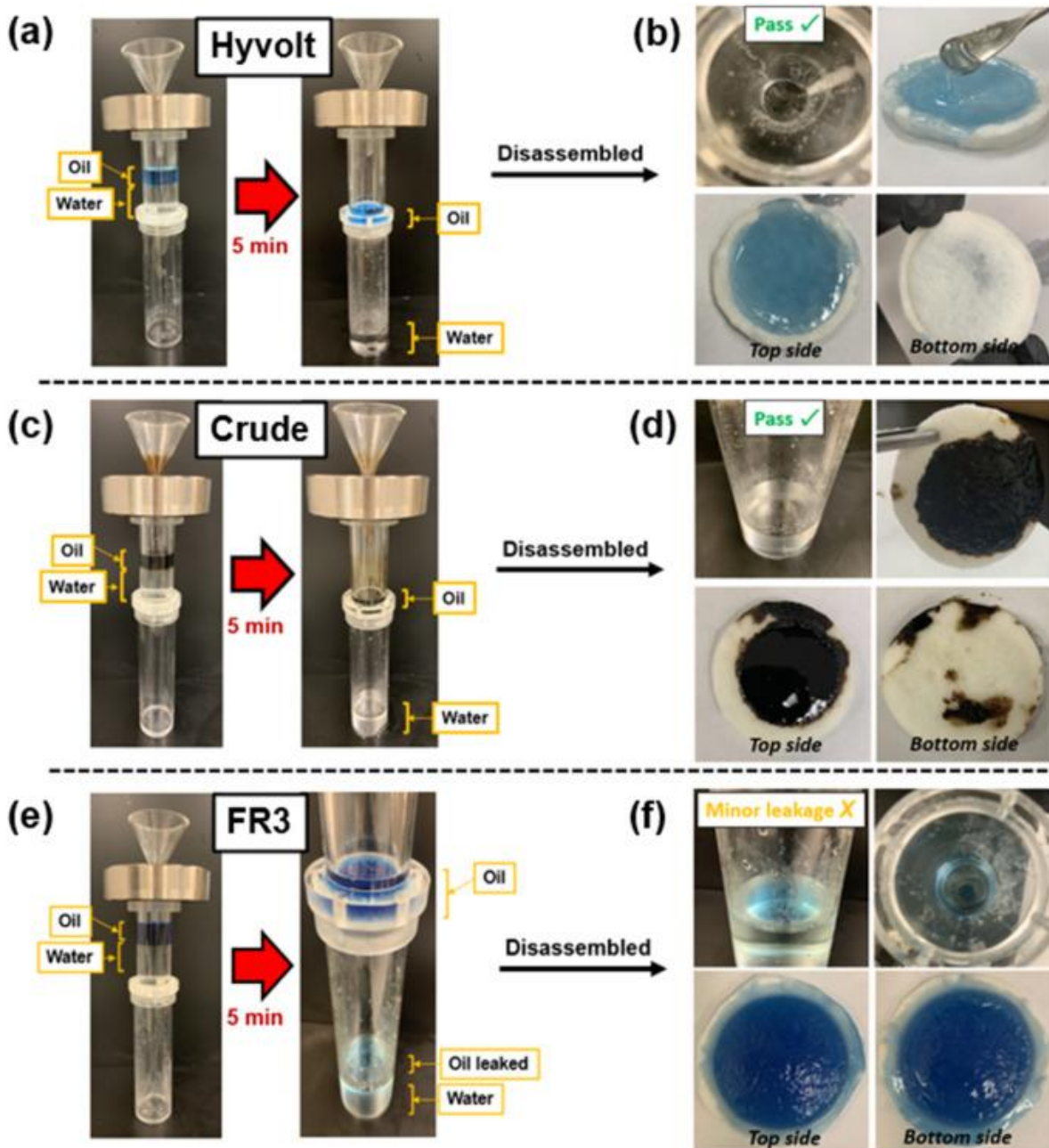


Figure 3.9. Oil-water filtration of SEBS fibers with various type of oils. Filtration system and disassembly of the SEBS fiber mat with (a) Hyvolt oil, (b) Crude oil and (c) FR3 oil. The SEBS fiber mat gelled well with Hyvolt and Crude oil and present oil leakage, while the gelation with FR3 is not efficient enough to block FR3 and cause minor leakage.

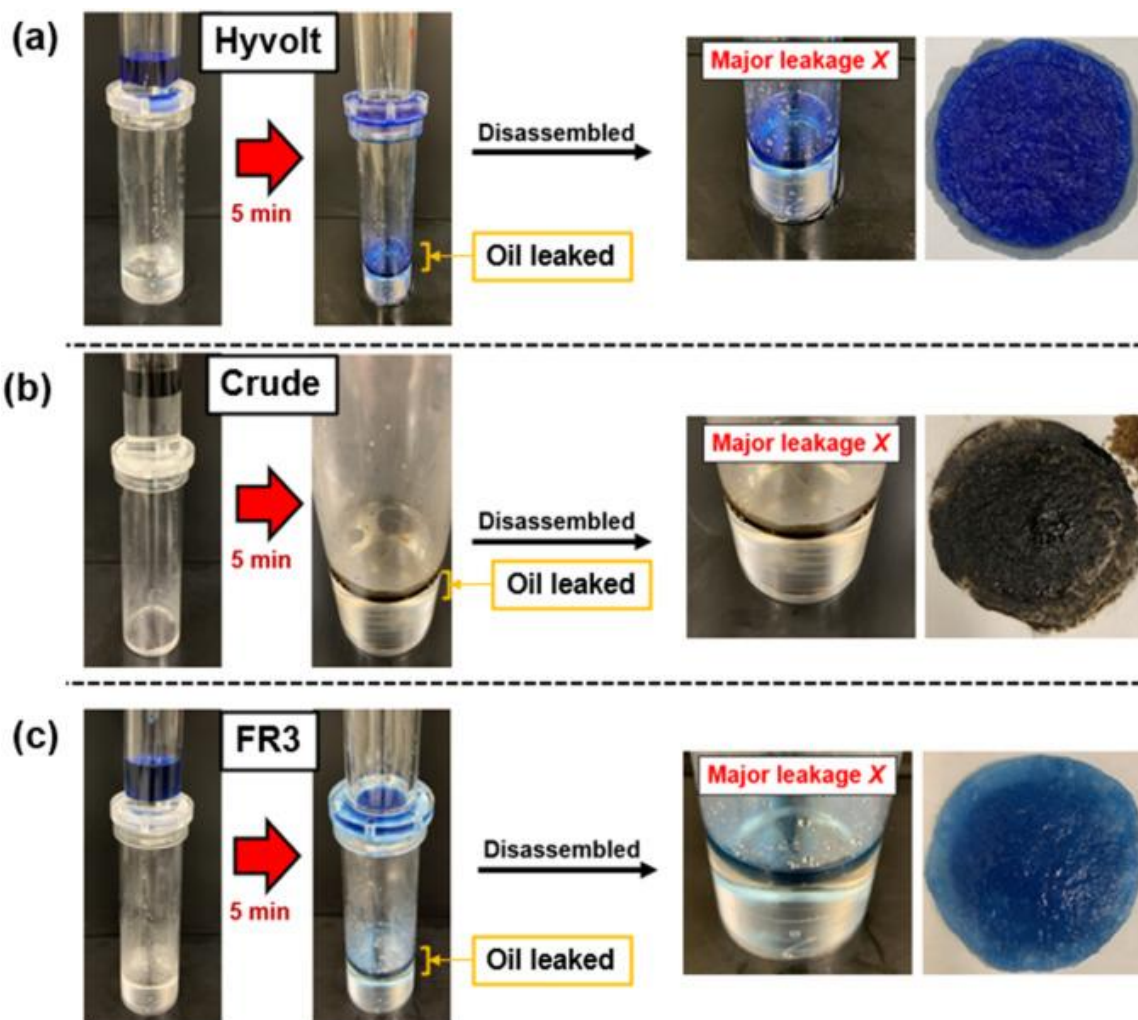


Figure 3.10. Oil-water filtration of PP fibers with various type of oils. Filtration system and disassembly of the PP fiber mat with (a) Hyvolt oil, (b) Crude oil and (c) FR3.

After initial sorption was examined, the effect of time was added to observe changes in the dominant oil sorption mechanism. SEBS fabrics were exposed to a 1:5 (fiber: oil) mass ratio for 24 h. PP was omitted from this study as its interaction with the oils have been shown to be adsorption, and therefore time has minimal or no effect on the interaction between the two. The result indicated that the Hyvolt oil and crude oil both created a thick gel with SEBS that

captured all the oil at ratio 1:5 (fiber: oil) after 24 h as seen in **Figure 3.8(b)**. This demonstrates that the dominant mechanism for oil retention transitions from adsorption and capillary forces to gelation given sufficient time of SEBS. This allows for the rubbery ethylene-butylene midblock to absorb the oil, essentially dissolving it in the oil. The glassy styrene end blocks, which are not soluble act as a crosslinker, giving the gel a solid-like consistency. The only oil that did not demonstrate this phenomenon was the FR3 oil as the poor interaction with the SEBS fibers does not allow for gel creation within a reasonable timescale. Furthermore, the initial elastic behaviour of the SEBS that allowed for higher initial sorption relaxes over 24 h, squeezed oil that initially been adsorbed in the fabric oozed out. This resulted in only 200% oil captured after 24 h. As noted, this gelling mechanism of SEBS non-woven fibers are only unique to this TPE due to the co-block structure. The PP fibers did not seem to possess such ability, which can give SEBS an edge in water-oil separation processes.

The strong hydrophobic/lipophilic properties of the SEBS nonwoven fabric and similar to PP nonwoven fabrics demonstrates a strong possibility for its use in oil spill remediation efforts. To demonstrate real world practicality, each oil was placed on top of water to examine the fabric's efficiency of removal. The fabric was immersed in the oil – water mixture for 30 s before removal. **Figure 3.8(d)** shows the clarity of the surface after the test. Both the Hyvolt oil and crude oil were successfully removed with the SEBS nonwoven fabric, leaving no trace of oil behind. On the contrary, the PP non-woven fabric was unable to remediate all the oil present, leaving a thin oily film on the surface of the water, as observed in **Figure 3.8(d)**. The SEBS fabric when used on the FR3 oil also left behind an oily film on the surface of the water.

The improved success of oil remediation with the SEBS nonwoven fabrics with different oils demonstrates superior oil selectivity compared to the PP nonwoven fabric. While the PP fabric has a greater initial sorption capacity than SEBS, it is less selective in its sorption of water. The superior performance of pure SEBS non-woven fibers was attributed to its enhanced oil trapping capabilities through oil gelation mechanism, which prevented the desorption of oil and allowed the SEBS non-woven fiber to retain the oil in the structure.

3.3.3.4 Oil and water selectivity

As a proof of concept, the exceptional oil–water separation of the SEBS nonwoven fabrics was evaluated through a gravity-driven filtration test conducted using a custom setup (**Figure 9**). Each nonwoven fabric was pressed between two tubes with a heavy weight to mitigate leakage from the sides. Approximately 75 mL of water was then poured overtop of the mat, followed by 25 mL of oil. The weight of the oil, the high porosity of the fabrics, and the inferior interaction of the hydrophobic polymers with water, allowed the water to pass through the fabrics while the oil was ad/absorbed via the fibers. In this application, the nonwoven fabrics acts as a filter to allow clean water to pass through. The goal of this test was to observe the ability of the nonwoven fabric to prevent the flow of additional oil after reaching its saturation point while simultaneously observing the mechanical strength of the fabric after gelation has occurred. The PP fabric was unable to stop any additional oil beyond its sorption capacity, causing much of the oil from each run to drip out the bottom. This can cause major problem as the transport of these fabrics away from an oil spill site could lead to additional pollution if the oil cannot be firmly immobilized.

On the other hand, the SEBS fabric effectively created a gel that sealed off any escape for the unabsorbed Hyvolt and crude oil. Furthermore, the reaction was quick enough that oil did not even completely penetrate the fabric before the gel was able to form, leaving the bottom side of the fabric completely dry, as shown in **Figure 9**. This fast gel formation is very desirable not only for the quick clean removal of oil from a contaminated environment, but also as a method of containing a spill to a smaller area if the fabrics were used in a preventative capacity as the gel is viscous and solid enough to seal the porous structure and inhibit further flow of oil. Even when tested with FR3 oil, only a small leak was detected, and the fabric was able to provide sufficient support that the not all oil seeped through the fabric. Nevertheless, the sealing mechanism of SEBS can be beneficial for oil/water separation applications, including geotextiles, which has advantages over the non-woven fiber of PP, in which the non-woven PP fabric fails to capture the oil due to the absence of gelation mechanism and allow major leakage through the bottom for all types of tested oil, as observed in **Figure 3.10**.

3.4 Conclusion

This study provided insight into the fabrication of pure SEBS melt blown nonwovens, a scarcely studied field of research. SEBS tri-block thermoplastic elastomer was successfully processed into fine continuous fibers for the fabrication of a porous nonwoven fabric using a customized laboratory-scale melt-blowing extrusion process. It was found that this fabric, when exposed to different types of oils, exhibited varying levels of interaction that led to different final material consistencies. Hyvolt mineral oil and crude oil dissolved well the ethylene-butylene midblock, leading to a thick, solid gel like consistency while FR3 vegetable

based diester fluid showed limited interaction with the fabric, leaving the fibers in the same elastic state as they started in. Gasoline and diesel were able to completely dissolve the styrene end blocks of the copolymer, as well as the ethylene-butylene midblock, meaning that they were of little interest for future applications. The gel formation phenomenon observed by the dissolution of the ethylene-butylene midblock allowed for superior oil – water selectivity and oil capture compared to PP, which is widely used in industry. In conclusion, the oil sorption and oil immobilization capabilities of SEBS, paired together with the large surface area of fabricated SEBS nonwoven fabrics was exploited to accomplish excellent oil selectivity that can be used for oil spill remediation and immobilization.

Chapter 4: 3D-printed, flow-through water filters for microplastic capture: the effect of surface porosity, column height, and pressure-sensitive adhesives on removal efficiency

4.1 Introduction

Microplastic pollution is an increasingly prevalent issue in the world today, with more and more scientists referring to it as the “Microplastic Crisis.” [178] With an estimated 4.8-12.7 million metric tonnes of mismanaged plastic waste finding its way into water bodies alone each year [179], it is perhaps unsurprising that microplastics have been found on every corner of the earth and in every facet of our daily lives. From the top of Mount Everest to the bottom of the Mariana Trench [180,181], and in the food, water, and air that enter our bodies [182–184], microplastics have become unavoidable and pose a serious threat to human health [185–188]. Microplastics are usually classified as solid synthetic materials ranging from 1 μm to 5mm in size [189,190]. Primary microplastics are those that enter the environment at the micron level, such as those found in toothpaste, facial cleansers, laundry effluent, industrial wastewater, and countless more [191,192]. Secondary microplastics, on the other hand, are formed by the physical, chemical, and biological erosion of plastic debris that is already persistent in the environment, causing fragmentation [193,194]. Many common microplastics are commodity plastics such as polyethylene (PE), polystyrene (PS), polyvinyl chloride (PVC), polyethylene terephthalate (PET), and polypropylene (PP) [195]. It is important that the issue of microplastic contamination is addressed while considering the sustainability of the solution. Therefore, the

utilization of biopolymers that do not accumulate in the environment and additives that are generated from a circular economy are of great scientific interest [196].

Poly(lactic acid) (PLA) is a biodegradable, aliphatic, and linear polyester thermoplastic that can be synthesized from biomass feedstocks such as sugarcane, corn, and starch [197–199]. Its high tensile strength and modulus [200], transparency [198], ease of processability [197], and compostability [201] have attracted significant attention in recent years, both in industry and the scientific community [202,203]. PLA has also become the polymer of choice in additive manufacturing (AM) or three-dimensional (3D) printing, an increasingly popular form of fused deposition modeling (FDM) where material is added layer-by-layer, usually through melt extrusion, for the creation of complicated 3D structures [204,205]. Excellent stiffness, high strength, low thermal expansion, and low ductility allow PLA to create high-resolution 3D prints that maintain their desired shape while maintaining their biodegradability, making it very desirable for such applications [206].

FDM printing offers high levels of control over the geometry of the final product, making it a low cost, easy to use option for the creation of porous, functional filters for the removal of microplastics from wastewater systems [207,208]. So far, limited research has been conducted on the usage of biopolymers as the feedstock for 3D-printed water treatment systems [209]. Of these systems, many rely on adsorption of the target analyte, and therefore require the filter to be completely submerged and perturbed to allow for sufficient time for adsorption to occur [210–215], which is both time-consuming and cost-ineffective. On the contrary, pour-over, flow-through filtration systems are gravity-fed, allowing them to be attached to a wastewater

supply line and left unattended with minimal hindrance to the output of the system. The issue with flow-through systems is the limited time the filters have to interact with the targeted analyte as it passes through. Physical interactions have historically been relied upon as the main mechanism of microplastic capture for flow-through devices developed for the filtration of textile wastewater [216,217]. However, these devices are only capable of modest filtration, with the two top performers of one study, XFiltr and GuppyFriend, displaying 78% and 54% microplastic removal efficiency, respectively [218].

This study explores various methods aimed at improving the non-covalent, physical interactions between microplastics and the 3D-printed, flow-through filters. Surface roughness and increasing surface area is a simple yet effective method of ensnaring small particulates on a surface by increasing the likelihood of it being lodged in the defect. Thermally induced phase separation (TIPS) has long been used to generate porous structures capable of size exclusion and reducing surface uniformity [40], but this is a solvent- and labour-intensive process. Recently, the creation of porous polymeric materials was demonstrated through the selective etching of a sacrificial additive post-processing [128]. This process was solvent-free, as it only required water for the creation of pores $< 2\ \mu\text{m}$ in size capable of improving air particulate filtration. Non-covalent interactions can also be improved through improved surface chemistries. Various functional fillers such as graphene oxide (GO), chitin, and metal-organic frameworks (MOFs) have been shown to improve interactions perceived by the microplastics [219–221]. Pressure-sensitive adhesives (PSAs), characterized by their low glass transition temperatures (T_g), are a class of polymer that can be easily deposited on a variety of substrates

and quickly wet and adhere to said surface. This makes them a very interesting option for microplastic removal, but they have so far been scarcely studied for such an application [222,223].

As a result of these discoveries and shortcomings, an examination into water-etched porous structures and PSA coatings was performed to examine their effect on flow-through microplastic capture. Due to the uncertain size of some previously reported filtration systems, the effect of filtration column height was also examined to visualize the maximum removal efficiency of each system.

4.2 Materials and methods

4.2.1 Materials

The PLA used in this study was Luminy LX175 extrusion grade PLA, supplied by TotalEnergies Corbion with a density, melt flow index (MFI), and molecular weight (MW) of 1.24 g/cm³, 8 g/10min at 210 °C/2.16 kg, and ~175 kDa, respectively. Polyethylene glycol (PEG) with an MW of 400 Da, poly(2-ethylhexyl acrylate) (P2EHA) with an MW of 92 kDa in 50% toluene, polystyrene with an MW of 350 kDa, dopamine hydrochloride, ammonium persulfate, Nile Red fluorescent dye, polysorbate 20 (Tween 20) non-ionic surfactant, tris base, acetone, and tetrahydrofuran (THF) were obtained from Sigma Aldrich (Oakville, ON, Canada). Cloisite 20A organophilic phyllosilicate nanoclay (NC) was purchased from Southern Clay Products (Texas, USA).

4.2.2 Sample preparation

4.2.2.1 Melt compounding

The PLA-PEG blends were melt-compounded with a twin-screw mini-extruder (Process 11, Thermo-Fisher Scientific) equipped with designated mixing zones. NC was added to all formulations as a rheology modifier and to aid with mechanical properties [201,224], allowing for higher PEG loadings to be processed properly. All formulations were processed using a temperature profile of Die-(190-195-200-200-190-190-100 °C)-Feeder and with a screw speed of 75 rpm. All formulations are listed in **Table 4.1**. Post extrusion, all filaments were ground into smaller pellets with an IKA grinder. Thin films with the dimensions of 75 x 76 x 0.2 mm were then produced using a Carver 4386 CH Laboratory manual heated hydraulic press. The thin films were processed at 180 °C and 5 metric tons for 3 minutes. The pressure of the press was ramped in 1 metric ton increments, followed by a pressure release, to prevent the formation of air bubbles in the created films prior to the 3-minute processing hold.

Table 4.1. Formulation composition for PLA 3D printing feedstock.

Sample	Formulation Composition (PHR)		
	PLA	PEG	NC
PLA	100	0	2
PLA-PEG5	100	5	2
PLA-PEG10	100	10	2
PLA-PEG15	100	15	2

4.2.2.2 3D printing

The filter design used in this paper was designed on SolidWorks. The filter design is comprised of two circular filters with an offset grid design of 1 x 1 mm square holes, as shown in **Figure 4.1a**. Each filter is 39 mm in diameter and 1 mm in height, with a 2 x 2 mm spacer around the edge to allow for a gap between filter layers. The offset grid design was used to increase tortuosity and maximize the surface area of the filter that is contacted as water flows through the filter. Each filter has a notch on the outside that fits into an inverted notch in the filter holder, as seen in **Figure 4.1b**. This ensures that the grid pattern is properly aligned to achieve the desired flow pattern. The repeating layers design allows for tunable filtration in the number used, depending on the contamination level of the water.

All 3D-printed filters were created using a G5 Pro pellet-based FDM printer from PioCreat 3D. Stereolithography (.stl) files from SolidWorks were converted into printer-readable geometry code (.gcode) files using the Creality Print slicing software. Optimized printing parameters were established and transferred to the G-code file using Creality Print and are displayed in **Table 4.2**.

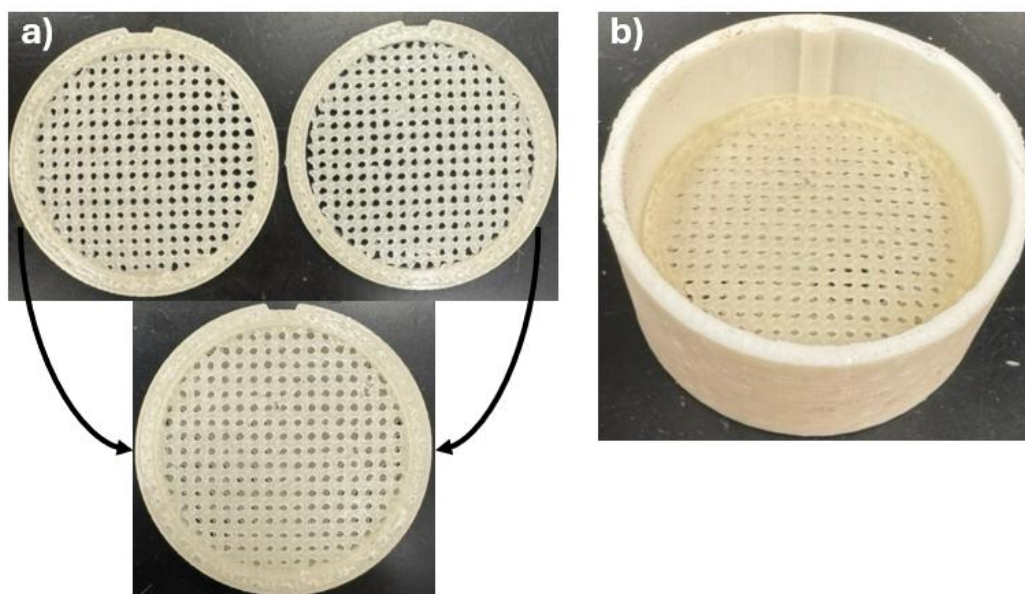


Figure 4.1. Schematic showing (a) the offset filter grid design and (b) the holder used to ensure the proper orientation of the grid during filtration.

Table 4.2. 3-D printing parameters from the Creality Print slicing software.

Printing parameter used	
Dimensions [L x W x T] [mm]	87 x 41 x 2
Nozzle Temperature [°C]	210
Bed Temperature [°C]	65
Print Pattern	Lines
Layer height [mm]	0.10
Line width [mm]	0.40
Infill density [%]	100
Print speed [mm/s]	50

4.2.2.3 Filter etching

Due to the poor compatibility of PEG in PLA attributed to polarity difference, it was expected to preferentially form spherical agglomerations within the PLA during melt processing [128]. This phenomenon can be leveraged by etching away the exposed PEG on the surface of the PLA, generating micro/nanopores and increasing the roughness of the surface of the filters. Etching was carried out by submerging the filters in boiling water for 1 hour to dissolve away the PEG without compromising the structural integrity of the PLA matrix. This process was repeated three times, with fresh water being utilized each time. After etching was completed, the filters were dried at 60 °C in an oven for 24 hours to ensure complete removal of moisture from the etching process.

4.2.2.4 PSA coating

Two different PSA coatings were examined in this study, P2EHA and polydopamine (PDA). The P2EHA coating was applied by first diluting the 50% P2EHA in toluene solution down to 10% using THF. THF was selected as the diluting solvent to prevent the precipitation of the P2EHA from the toluene, while also having low dissolution strength over PLA, especially at room temperature. The filters were submerged and lightly stirred in the P2EHA solution for 30 seconds, then removed and placed in an oven at 60 °C overnight to remove any residual solvent from the coating.

The PDA coating was deposited on the PLA filters through the oxidative self-polymerization of dopamine hydrochloride. A 0.5 M tris buffer with pH = 10 was prepared, and 0.0528 M of ammonium persulfate was added as an oxidant. The filters were suspended in a cheesecloth, submerged in the buffer, then 0.0264 M of dopamine hydrochloride was added to the buffer to start the reaction. The reaction was left to proceed for 24 hours under moderate stirring at room temperature. The filters were then removed, rinsed to remove any unreacted dopamine and buffer solution, then left to dry in oven at 60 °C overnight.

4.2.3 Parallel plate rheology

To observe the change in processability from increasing PEG loading, rheology was conducted using a HAAKE MARS III rheometer equipped with a rotating parallel plate geometry (1 cm diameter disc at 1 mm gap width). Tests were run in accordance with the ASTM D882-18 standard and at 200 °C. An oscillation frequency test was conducted over an angular frequency range of 0.1–100 Hz and at a strain of 0.01 %, well within the linear visco-elastic region for PLA. Storage modulus (G'), loss modulus (G''), and complex viscosity ($|\eta^*|$) were taken from the conducted tests.

4.2.4 Differential Scanning Calorimetry (DSC)

Thermal analysis of the PLA-PEG blends was conducted using a TA DSC2500 differential scanning calorimeter (DSC) equipped with an autosampler. Samples (~10 mg) were placed in aluminum T_{zero} pans and subjected to a heat/cool/heat cycle from 0-200 °C at a ramp speed of 10 °C under constant nitrogen flow (50 mL/min). All analyses were performed using the second heating cycle.

4.2.5 Filter characterization

4.2.5.1 Fourier transform infrared spectroscopy (FTIR)

A ThermoScientific Nicolet 6700 model Fourier transform infrared spectrometer (FTIR), equipped with a GladiATR attenuated total reflectance (ATR) apparatus, was used to verify the removal of PEG through the etching process, as well as to verify the deposition of PDA and P2EHA during the PSA coating process. The spectra were collected in absorption mode between 500-4000 cm^{-1} with a resolution of 4 cm^{-1} and 64 scans.

4.2.5.2 Mechanical testing

Tensile testing was conducted on regular and etched PLA-PEG films to observe the varying mechanical properties from increased PEG loading and etching. A Shimadzu – AGS X Universal Testing Machine, equipped with a 500N load cell, was used to determine tensile strength, tensile modulus, and elongation at break. The tests were performed in tensile mode at room temperature at a crosshead speed of 10 mm/min and an initial gauge length of 50 mm. The elastic modulus was taken from the linear elastic region of the tensile test according to Equation (4.1):

$$\varepsilon = \frac{\Delta F/A}{\Delta L/L_0} \quad (4.1)$$

4.2.5.3 Microscopy

A field emission scanning electron microscope (FESEM) (FEI Quanta Feg 250) was used to examine the surface topography of the 3D printed filters before and after etching. Samples were observed at 65x, 350x, 1500x, and 8000x magnification and at a voltage of 10kV.

4.2.6 Microplastic filtration and quantification

A PS microplastic dispersion was created by first milling PS pellets with a Retsch ZM 200 centrifugal mill equipped with an 80 μm sieve at 16000 rpms. These microplastics were then stained with Nile red, a fluorescent dye commonly used in protein tagging, according to the protocol established by Maes et al. [225], washed thrice with water through vacuum filtration, and let dry overnight in an oven at 60 °C. The dyed microplastics were dispersed in water at 100 ppm along with 2.24 mM of Tween 20 to improve dispersion and prevent agglomeration.

A gravity-driven filtration method was selected in this study as a practical method for evaluating the filtration efficiency of the fabricated filters. The 3D printed filters were stacked on top of each other, wrapped in parafilm to avoid water leakage out of the side, and secured within the filter holding column (shown in **Figure 4.2**). 100 mL of microplastic-contaminated water was poured through the filter and collected below for further characterization.

Filtration efficiency of all fabricated filters was quantified using fluorescent spectrophotometry (Cary Eclipse Fluorescence Spectrophotometer, Agilent Technologies). An excitation wavelength of 560 nm was used, and the emission spectra was scanned from 500-800 nm. A calibration curve of maximum emission intensities was created from 10-150 ppm microplastic suspensions to predict the concentration of microplastics present before and after filtration.

To obtain a representative particle size distribution of the microplastic dispersion, an Olympus BX53M polarized optical microscope (POM) was utilized. A 10 μL drop from the filtered and unfiltered water was placed on a glass cavity slide and examined at 20x magnification. The 3D-printed filters were also imaged using an EVOS fluorescence microscope at 10x magnification to better visualize the microplastics on the surface of the filter after filtration.

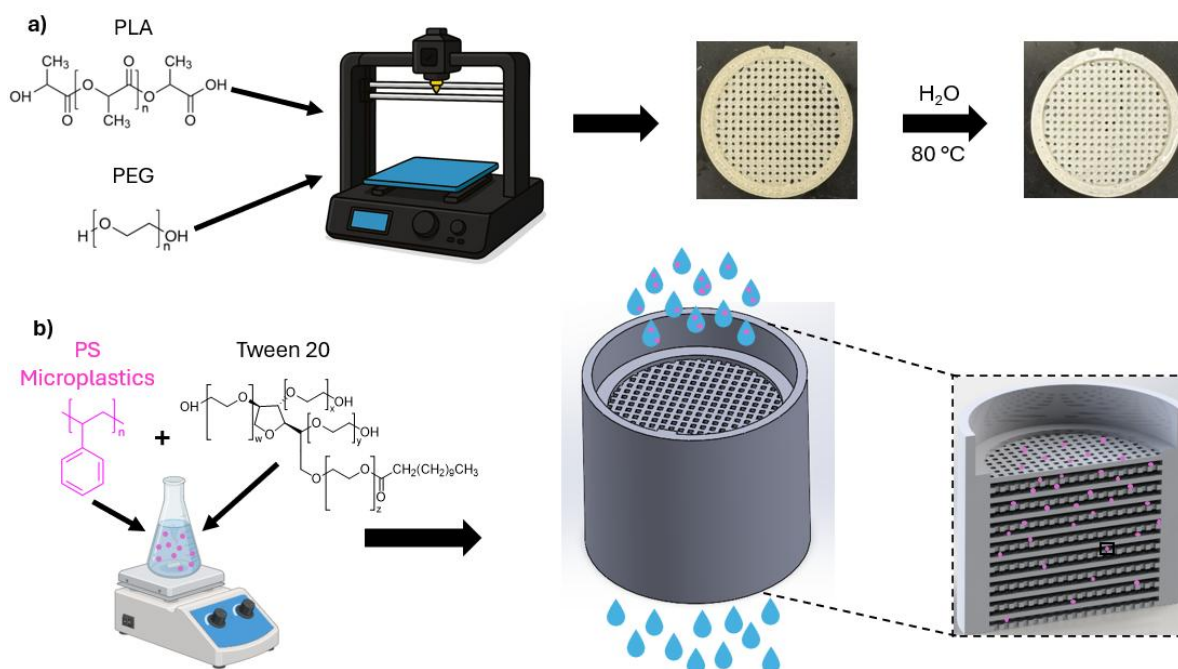


Figure 4.2. A schematic procedure of the (a) filter preparation and (b) microplastic filtration.

4.3 Results and discussion

4.3.1 Verification of etching process

FDM printing is known for its ability to generate sleek and glossy finishes on its manufactured parts. The relatively low melt strength and high MFI of PLA make it an ideal candidate for FDM printing. However, for physical interaction microplastic capture, smooth surfaces are

disadvantageous. Therefore, it was essential to be able to demonstrate successful pore creation through PEG etching prior to its application for such endeavours. Low molecular weight PEG (400 Da) was selected for blending due to its higher water solubility and lower miscibility in PLA [128,226]. These attributes allow it to be dissolved from the printed filters more easily and at lower temperatures, lowering the risk of damaging or warping the filters during the etching process. Less miscible phases are also more likely to aggregate into more defined domains in the PLA matrix. This means that only the surface-exposed PEG will be subjected to the etching process, and the filters will be less susceptible to percolation effects of the etched PEG that could unnecessarily reduce the mechanical strength of the filters.

FTIR spectra before and after 3 rounds of hot water etching are shown in **Figure 4.3a**. Characteristic peaks of PLA at 2995 cm^{-1} (-C-H stretching), 1750 cm^{-1} (-C=O stretching), 1180 cm^{-1} (-C-O stretching), and 1047 cm^{-1} (-O-H bending) were identified in the reference spectrum [128,227]. Characteristic peaks of PEG at 3420 cm^{-1} (-O-H stretching), 2866 cm^{-1} (-CH₂- stretching), 1092 cm^{-1} (-C-O-C- stretching), and 900 cm^{-1} (-C-H bending) were similarly identified in the reference spectrum [128,228]. The PLA-PEG blends, seen clearly in **Figure 4.3b**, more closely resemble the spectrum of PLA, the dominating phase of the blend, but PEG peaks are still visible with lower peak intensities. The clearest changes seen between pre- and post-etching blends are peak reductions at 3420 cm^{-1} (-O-H stretching), 2866 cm^{-1} (-CH₂- stretching), and 900 cm^{-1} (-C-H bending), all of which are contributed by the PEG phase. Another change observed was the narrowing of a peak found in the fingerprint region around $600\text{-}700\text{ cm}^{-1}$. This change could be due to the reduced contribution of a broad peak found

between $\sim 530\text{-}680\text{ cm}^{-1}$ in the fingerprint region of PEG [229], further demonstrating its partial removal from the blends. The persistence of PEG in the PLA-PEG blends after the etching process is due to the thickness of the printed filters and the presence of PEG domains in the interior core of the filters. The poor miscibility of PEG leads to more isolated phases within the PLA matrix, meaning that a large amount of the PEG is protected from the etching process by the PLA surrounding it, and only the PEG present right on the surface is successfully etched away.

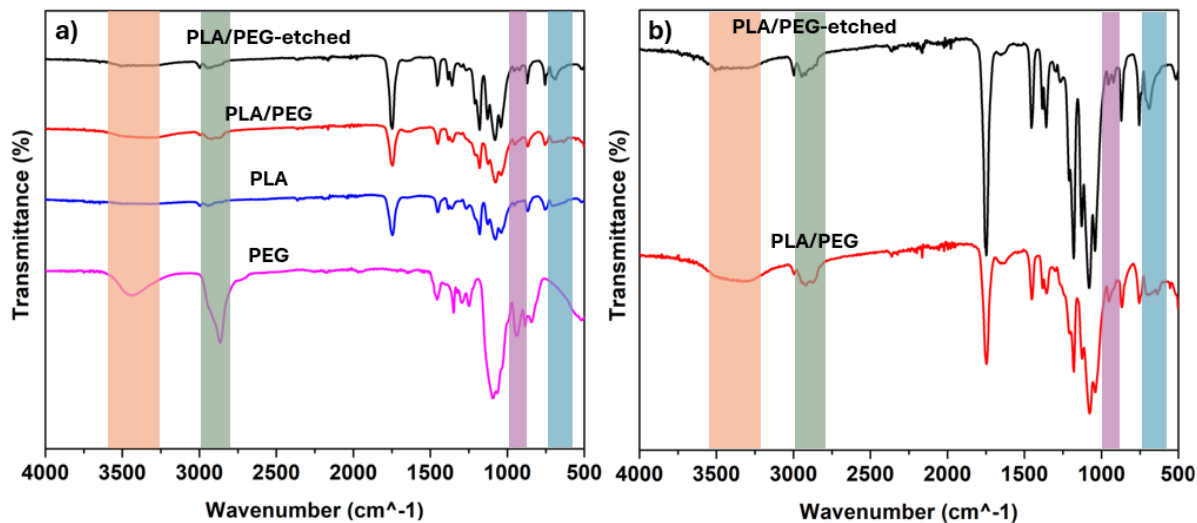


Figure 4.3. ATR-FTIR spectra of the PLA-PEG blend before and after the surface etching of PEG.

Figure 4.4 shows the surface morphologies and overall print quality of the PLA filters before and after etching. It can be seen that the etching process made no major dimensional or structural changes to the 3D-printed filters, as the grid lines and intersection points remain unaltered. However, with the SEM, nanopores as small as 100nm, and micropores as large as 5-10 μm can be seen on the surface of the filters in **Figure 4.4h**. Larger surface irregularities

~50 μm in size can also be seen in **Figure 4.4g**. All of these surface defects have the potential to catch microplastic fragments of assorted sizes as they come into contact with the surface due to increased roughness and available surface area. These images demonstrate well the mechanism of PEG etching as a method of generating micro- and nanopores on the surface of the 3D printed filters to enhance surface roughness.

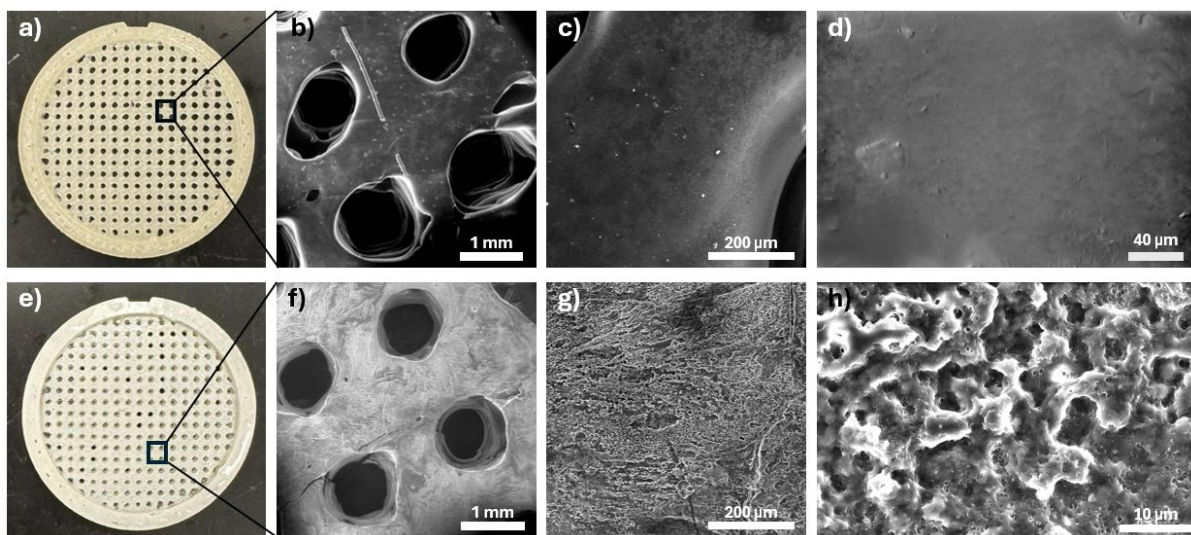


Figure 4.4. Pictures/SEM images of unetched PLA-PEG10 filters at a magnification of (a) 1x, (b) 65x, (c) 350x, and (d) 1500x. Pictures/SEM images of etched filters seen at (e) 1x, (f) 65x, (g) 350x, and (h) 8000x magnification.

4.3.2 Formulation optimization

The flowability and processability of a polymer feedstock are very important in FDM printing to ensure high-resolution prints. Therefore, parallel plate rheology was undertaken to examine the effect of increasing PEG content in the PLA-PEG blends. All blends in **Figure 4.5a** show a shear-thinning (pseudoplastic) behaviour, typical of thermoplastic polymer melts, as well as a notable decrease in complex viscosity with increasing PEG content. Low molecular weight

PEG acts as an external plasticizer by diffusing between the high molecular weight, low mobility PLA chains, reducing intermolecular forces and entanglement density, while generating more amorphous regions and higher free volume in the polymer melt [230–232]. All of these shifts in macromolecular structure can be attributed to reductions in viscosity, as the two concepts are highly correlated [233,234]. These changes can also be seen in the dynamic moduli shown in **Figure 4.5b**. Increasing PEG content delays the crossover modulus to higher frequency regions, leading to a shift to a viscously dominated flow behaviour across the entire studied range. This can be attributed to weakened intermolecular interactions, polymer entanglement, and decreased crystallinity from the PEG plasticization [230–234]. This is also concluded by decreases in magnitude in both the storage and loss moduli with increasing PEG loading.

A thermal analysis of the PLA-PEG blends was also conducted to examine how increased PEG loading impacted internal structure. The main thermal events observed on the second heating cycle were a glass transition (T_g), a cold crystallization (T_{CC}), and a melting peak (T_m), as shown in **Figure 4.5c** and **Table 4.3**. As seen in rheology, the blends with higher PEG loading display higher degrees of plasticization, having higher free volume and molecular mobility compared to the baseline PLA. This is seen in the shift of T_g and T_{CC} towards cooler temperatures, as less energy is required to initiate chain migration and crystal formation [235,236]. The effects of this are also seen in H_{CC} , which initially increases and then decreases. PLA is known for its slow crystallization kinetics [237], but the small addition of plasticizer may have led to faster and more complete crystallization, as the crystallization peak narrows

compared to the baseline, and is more distinctly separate from the onset of melting. However, as more PEG is added after this, steric hindrance and intermolecular blocking become more prominent, leading to decreased crystal formation and lower H_{CC} [237].

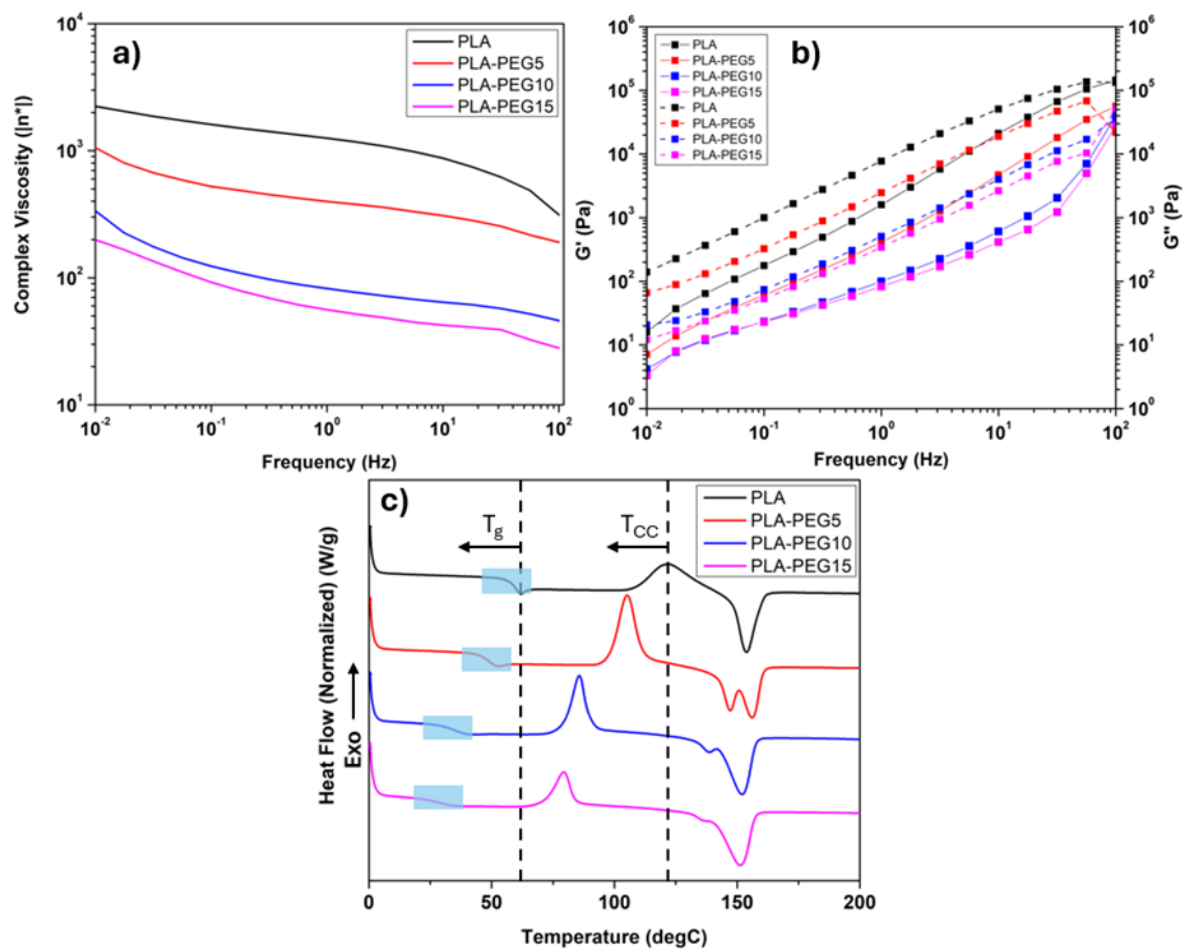


Figure 4.5. The (a) complex viscosity and (b) dynamic moduli of the PLA-PEG blends at varying PEG content obtained through melt rheology at 200 °C; (c) DSC thermograms of the PLA-PEG blends.

Table 4.3. Thermal properties of PLA and PLA-PEG blends obtained from DSC.

	T _g (°C)	T _{cc} (°C)	H _{cc} (J/g)	T _m (°C)
PLA	58.51	122.43	26.77	153.73
PLA-PEG5	47.76	105.73	33.21	155.11
PLA-PEG10	33.93	86.15	24.32	151.97
PLA-PEG15	29.20	79.67	16.01	151.19

The mechanical properties of the regular and etched PLA-PEG blends were examined using tensile testing and are shown in **Figure 4.6a-d**. Two clear trends, one for increasing PEG loading and the other for the transition from regular to etched samples, can be observed in the tensile data. From the baseline PLA to PLA-PEG15, increasing plasticity and weakened intermolecular interactions from PEG addition lowered the tensile strength from 46 MPa to 22 MPa and the elastic modulus from 2.13 GPa to 1.13 GPa, respectively [231,232]. An increase in ductility, from 3% strain at break to 34%, is also attributed to increased plasticization from the PEG. The removal of PEG through etching led to the deterioration of all mechanical properties, with higher PEG loading blends exhibiting the worst performance after etching. Increased porosity in the etched samples acts as microscopic voids that decrease the cross-sectional area of the samples and reduce the available material for stress transfer during testing. This can lead to a variety of stress transfer and stress concentration phenomena in the remaining polymer matrix that result in premature mechanical failures [238,239].

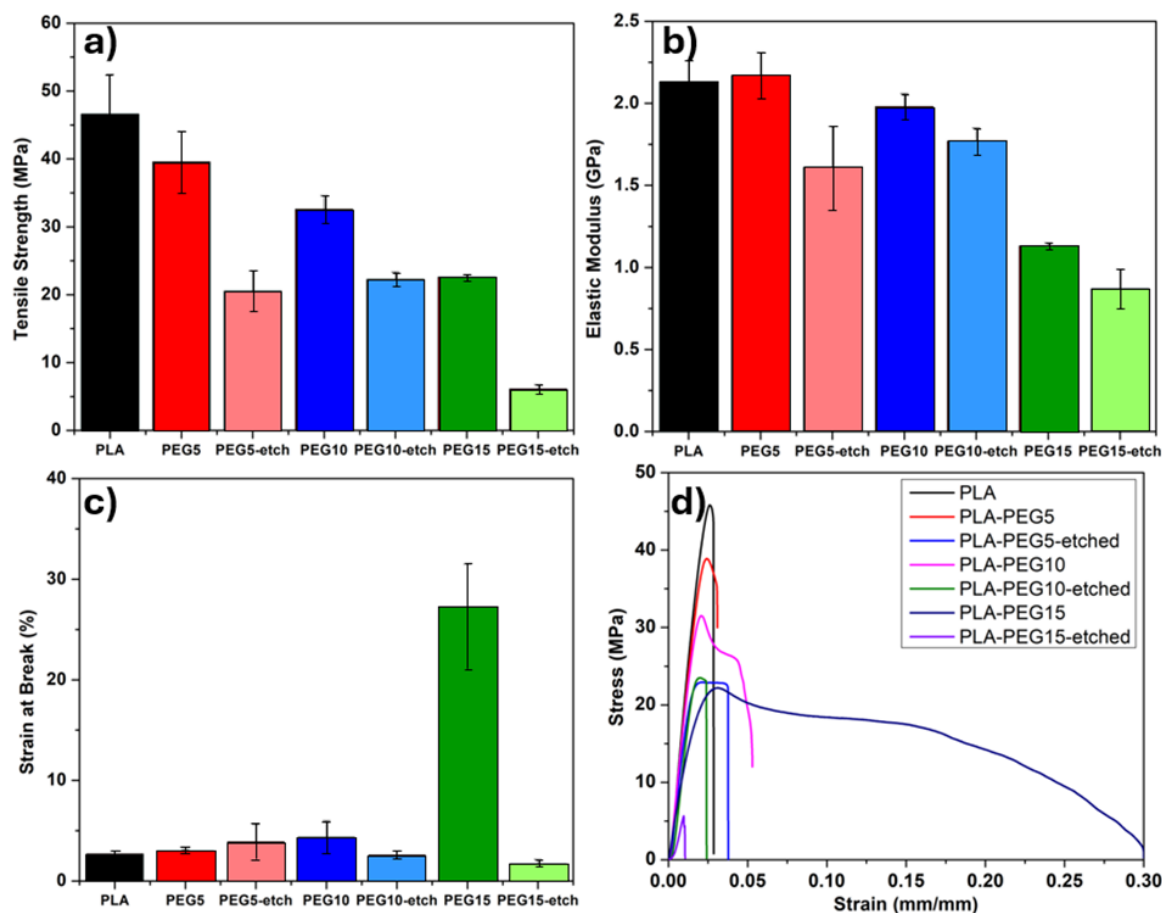


Figure 4.6. The (a) tensile strength, (b) elastic modulus, (c) strain at break, and (d) representative stress-strain curve for all etched and unetched PLA-PEG blends.

The surface morphology of all filters was examined via SEM and is shown in **Figure 4.7(a-n)**. The baseline PLA filter had a smooth surface yet displayed some surface roughness and print impurities owing to its significantly higher melt viscosity. PLA-PEG5 and PLA-PEG10 filters displayed better print quality owing to increased plasticity and flowability while maintaining the desired print dimensions and structure. PLA-PEG15 samples began to show signs of wall narrowing or filament necking, possibly as a result of overplasticization. It can also be seen at 350x magnification that the PLA-PEG15 sample has some micropores present on the surface,

even before the etching process. This could be a result of phase separation between the PLA and PEG while in the molten state due to poor miscibility and varying densities. It could also be a result of low levels of PEG degradation from extended exposure to heat, as the onset of 400 Da PEG degradation is $\sim 215^{\circ}\text{C}$ [240]. All etched filters showed no visible shrinkage as a result of the etching process, and the creation of micropores on the surface of the filters was observed in all samples. The etched PLA-PEG15 sample showed cracking on the surface of the filter as a result of insufficient remaining PLA to reinforce the remaining structure of the filter. The etched PLA-PEG10 sample displayed the highest level of surface roughness and porosity while maintaining its structural integrity.

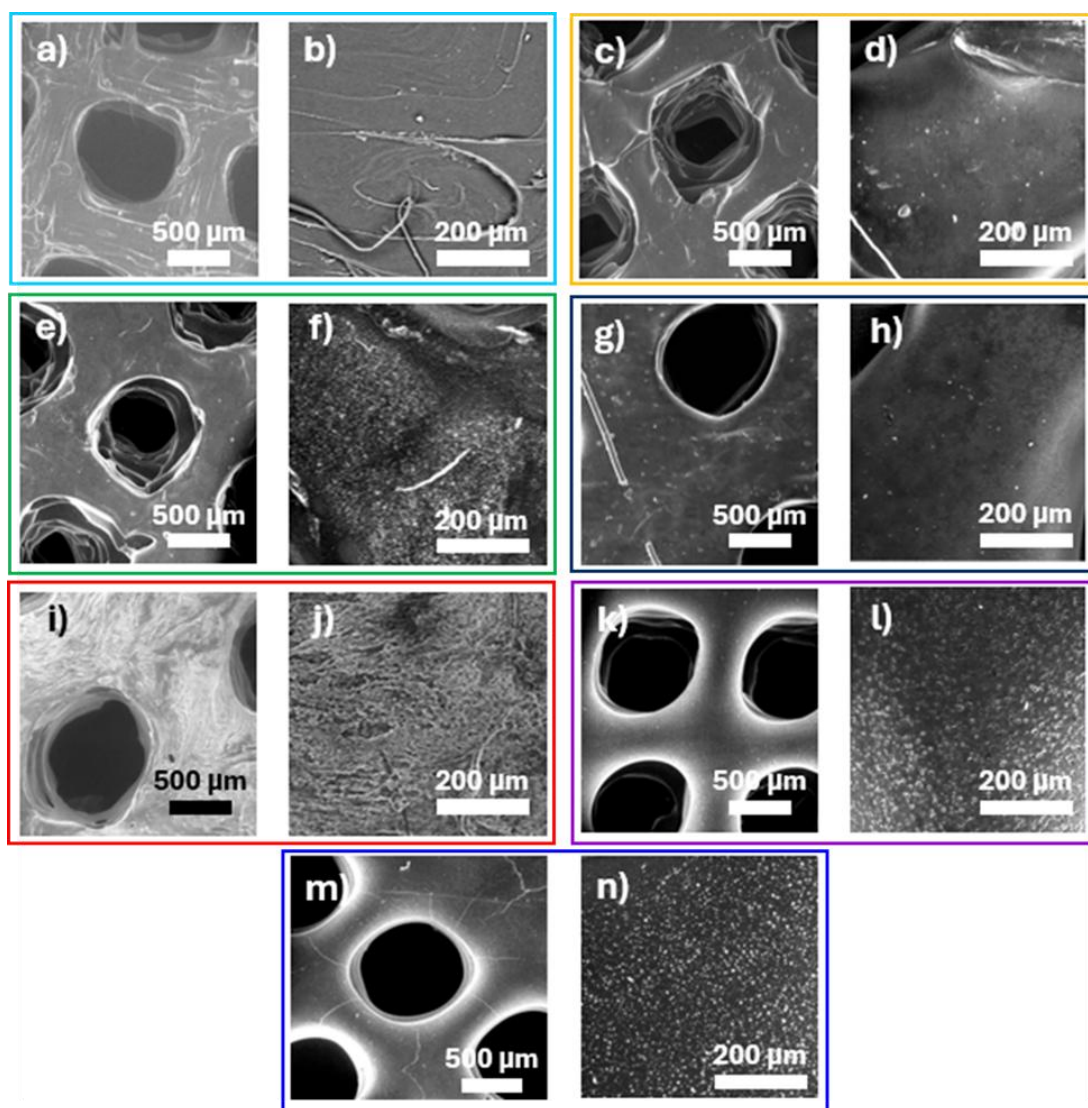


Figure 4.7. The filter surface morphology at 65x and 350x magnification for (a,b) PLA, (c,d) PLA-PEG5, (e,f) PLA-PEG5-etched, (g,h) PLA-PEG10, (i,j) PLA-PEG10-etched, (k,l) PLA-PEG15, and (m,n) PLA-PEG15-etched, respectively.

4.3.3 Microplastic filtration

After the initial screening of formulations, PLA-PEG10 was selected to be utilized for all remaining tests. It offered good resolution and processability for FDM printing, while still

maintaining acceptable mechanical properties required to withstand the etching process and subsequent filtration. All references to this baseline PLA-PEG10 formulation hereafter will be referred to simply as PLA, and PLA-PEG10-etched will be referred to as PLA-etched.

Two different pressure sensitive adhesives (PSAs) were chosen to be examined in this study. P2EHA is a common acrylic-based adhesive that relies on a low T_g ($-50\text{ }^{\circ}\text{C}$) and relatively high molecular weight to generate its tack, allowing it to stick to a large variety of substrates [241,242]. P2EHA can be synthesized from waste diapers as feedstock, contributing to a more circular economy [222,223]. It is also more polar than other elastomeric adhesives [242], giving it comparatively better wettability and interaction with water-based systems, while still residing in a similar range of surface energies seen in many commodity microplastics [222]. This means that P2EHA will adhere easily to the 3D-printed filters and have a strong affinity to any microplastics that come into contact with it. PDA, the other PSA chosen for examination in this study, has garnered much attention in recent years for its biomimicry of mussel adhesive proteins first demonstrated by Lee et al [243,244]. Its ability to attach to a variety of substrates, such as metals, oxides, ceramics, and polymers, along with its biodegradability, makes it a very interesting and increasingly studied coating and adhesive [244–246].

To validate the successful deposition of P2EHA and PDA on the surface of the PLA filters, FTIR spectra of the coated and uncoated filters were obtained and shown in **Figure 4.8**. The emergence of peaks at 3379 cm^{-1} ($-\text{O}-\text{H}$ and $-\text{N}-\text{H}$ stretching) and 1627 cm^{-1} ($-\text{C}=\text{O}$ stretching), highlighted in green, corresponds to prominent characteristic peaks of PDA, confirming its existence on the surface of the PLA [247,248]. Macroscopically, the surface of the filters also

transitioned from a translucent white colour to a deep brown colour. Similarly, the peak intensities at $2959\text{--}2858\text{ cm}^{-1}$ ($-\text{CH}_2-$ and $-\text{CH}_3$ stretching), 1750 cm^{-1} ($-\text{C}=\text{O}$ stretching), 1245 cm^{-1} (asymmetric $-\text{C}-\text{O}$ stretching), and 1165 cm^{-1} (symmetric $-\text{C}-\text{O}$ stretching) all greatly increase from the presence of P2EHA on the surface compared to the uncoated filter [249].

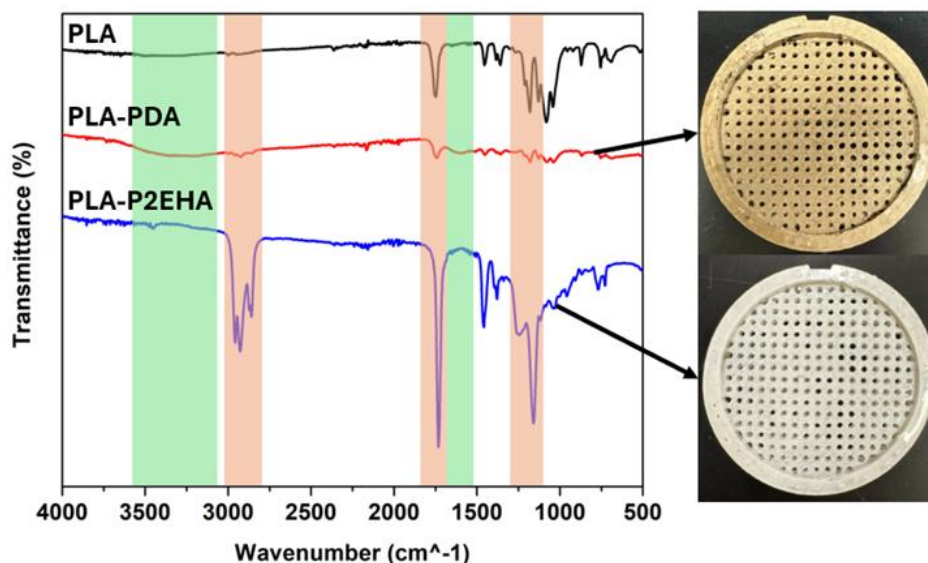


Figure 4.8. ATR-FTIR spectra of uncoated, PDA-coated, and P2EHA-coated PLA filters.

To accurately quantify the amount of microplastics captured by the filtration column, many different techniques (UV-Vis calibration curves, POM particle counting) were screened. Fluorescence spectrophotometry was eventually decided upon due to its consistency and ease of operation during initial trials. All ground PS microplastics were dyed with Nile red simultaneously for 3 hours to ensure all microplastics were stained equally. Nile red has an excitation spectrum from $\sim 450\text{--}650\text{ nm}$, and an emission spectrum from $\sim 550\text{--}800\text{ nm}$ [250]. 560 nm was chosen as the excitation wavelength, resulting in a peak emission wavelength of $\sim 630\text{ nm}$. The magnitude of the emission peak is proportional to the total surface area of stained

microplastics present in the sample. Therefore, the removal efficiency calculated in this work will be a measure of the total mass of microplastics removed, accounting for any particle size distributions present in the PS microplastics. The choice of using PS beads for this work was to give an accurate representation of how common commodity plastics like PS, polyolefins, and polyesters would interact with the designed system. The method of milling them down to the intended size was also selected to imitate the abstract morphologies and size distributions that would be seen in traditional contaminated water.

The first round of filtration testing evaluated the effect of surface modifications made to the filters in the filtration column, and the results are shown in **Figure 4.9a**. 8 Filters were selected as the column height to provide an adequate level of opportunity for physical attractions between the microplastics and the filters. The baseline PLA filters exhibited a limited removal efficiency of 16%. The smooth surface of the printed filter, paired with the limited physical interactions between the PLA and microplastics, likely led to many of the microplastics that initially contacted the surface sliding off or being washed off. The filter pore size also means that it is possible some microplastics were able to flow through the filter without coming into contact with the surface. The addition of the etching process greatly improved the filtration capability of the uncoated filters up to 37% removal efficiency. The rough, porous surface likely reduced the likelihood that any microplastics that came into contact with the filter surface would be washed off, as the microplastics would become lodged in the micropores. This should especially be true for microplastics $< 10\ \mu\text{m}$, as **Figure 4.4h** shows that most of the etched pores fall under this size. Therefore, it is still plausible that larger microplastics

would be capable of dislodgement from the filter surface, leading to the resulting low removal efficiency. The PSA coating process further improved microplastic capture, with the etched PDA filters capturing 46% of microplastics and the etched P2EHA filters capturing 51%, respectively. The adhesives provided tack to the filter surface, enhancing physical interactions felt by the microplastics from the filter surface. The difference in filtration between the two PSA coated systems comes down to the level of interaction that able to be generated and sustained by each respective adhesive. While not quantified, it is suspected that the molecular weight of the P2EHA adhesive is greater than that of the synthesized PDA adhesive, which has been shown to lead to better adhesive retention over longer periods [251,252]. This could be a possible reason for its superior performance.

Following these tests, it was decided that a closer look at the filtration column height was necessary to achieve enhanced removal efficiency with the 3D-printed system. Due to their performance in the previous test, the P2EHA-etched filters were utilized in this test over the PDA-etched filters. 8, 12, 16, and 20 filter high filtration columns were tested, and the results are shown in **Figure 4.9b**. A predictable trend is seen, with taller filtration columns producing higher removal efficiencies. Most notably, 20 etched, P2EHA-coated PLA filters were able to remove 90% of microplastics from the wastewater. This large boost in removal efficiency can likely be attributed to a couple of key factors that improved as the filtration column height was increased. A longer total flow time, paired with more total available surface area, would have greatly improved the probability of any given microplastic contacting and adhering to the surface of the filtration column. Both the baseline PLA filters and the etched PLA filters show

improved removal efficiency with increasing column height as well. However, with weaker physical attractions between each filter layer and the microplastics, the addition of more filter layers was less pronounced. Only 6% more microplastics were captured with 20 PLA filters compared to 8 PLA filters. Comparatively, an increase of 10% and 49% removal efficiency was seen with the etched and P2EHA-etched PLA filters, respectively. It is important to note that other factors, such as the existence of surfactant in the microplastic suspension (an artifact added to stabilize the microplastic suspension test samples), were not considered in this study and could lead to different interactions between the filter substrate, the PSA, and the microplastics. It has been speculated that surfactants could create a shielding effect for the charge present on the PS microplastic surface, and affecting the filtration operation [252].

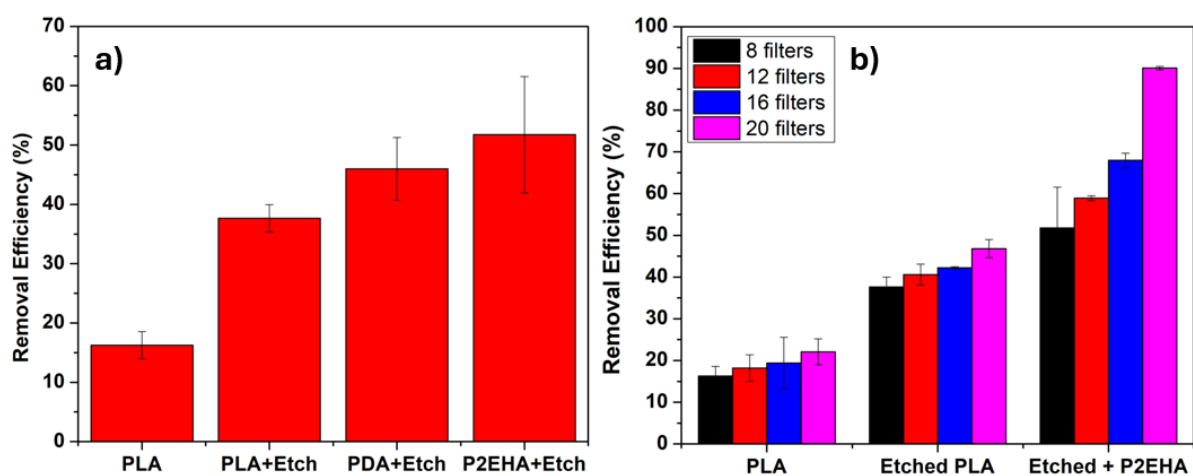


Figure 4.9. The effect of (a) surface morphology and PSA coating and (b) filtration column height on the efficiency of microplastic removal.

Following filtration, both the microplastic wastewater and the 3D-printed filters were examined to better understand the interactions that had taken place during filtration. Small

cross sections of the microplastic wastewater were examined under a POM microscope to generate a representative curve of the microplastic size distribution. **Figure 4.10a** shows the size distribution of the microplastics before filtration. Most of the microplastics, ~90%, were under 20 μm in size, with 43% of the microplastics being $< 6 \mu\text{m}$. The remaining 10% of larger microplastics were much broader in distribution, ranging from 20-280 μm in size. After filtration, the distribution curve shifts even further left towards smaller particle sizes, as shown in **Figure 4.10b**. 95% of the remaining microplastics are $< 20 \mu\text{m}$, with 80% being $< 10 \mu\text{m}$. This shows a clear lower limit to the size of microplastics that can be reliably captured with this filtration system, despite earlier assumptions about the size of particles captured within the etched pores. While the addition of the etched pores on the surface did substantially improve the filtration performance, this may have been accomplished through the ensnaring of larger microplastics than previously predicted from only considering pore size.

Small microplastics, often weighing 1-5 picograms in mass, do not generate much physical force from gravity, leading to weaker attractions with the surface. They are also more susceptible to turbulent flow that might cause them to never come in contact with a filter surface. Inversely, it can also be seen that almost all large microplastics were removed via filtration, with only 5% $> 20 \mu\text{m}$ and no microplastics seen larger than 50 μm . This is expected, as larger particles will be less susceptible to the phenomena mentioned above. They can also generate stronger physical impacts on the surface from gravitational pull, leading to stronger PSA adhesion. Fluorescence microscopy, shown in **Figure 4.10c-d**, corroborates the results seen in the POM particle size analysis. A filter from the middle of the filtration column was

selected for imaging. The microplastics seen on the surface after filtration are generally larger than 20 μm , in agreement with the disproportionate drop in $> 20 \mu\text{m}$ particles observed from particle counting.

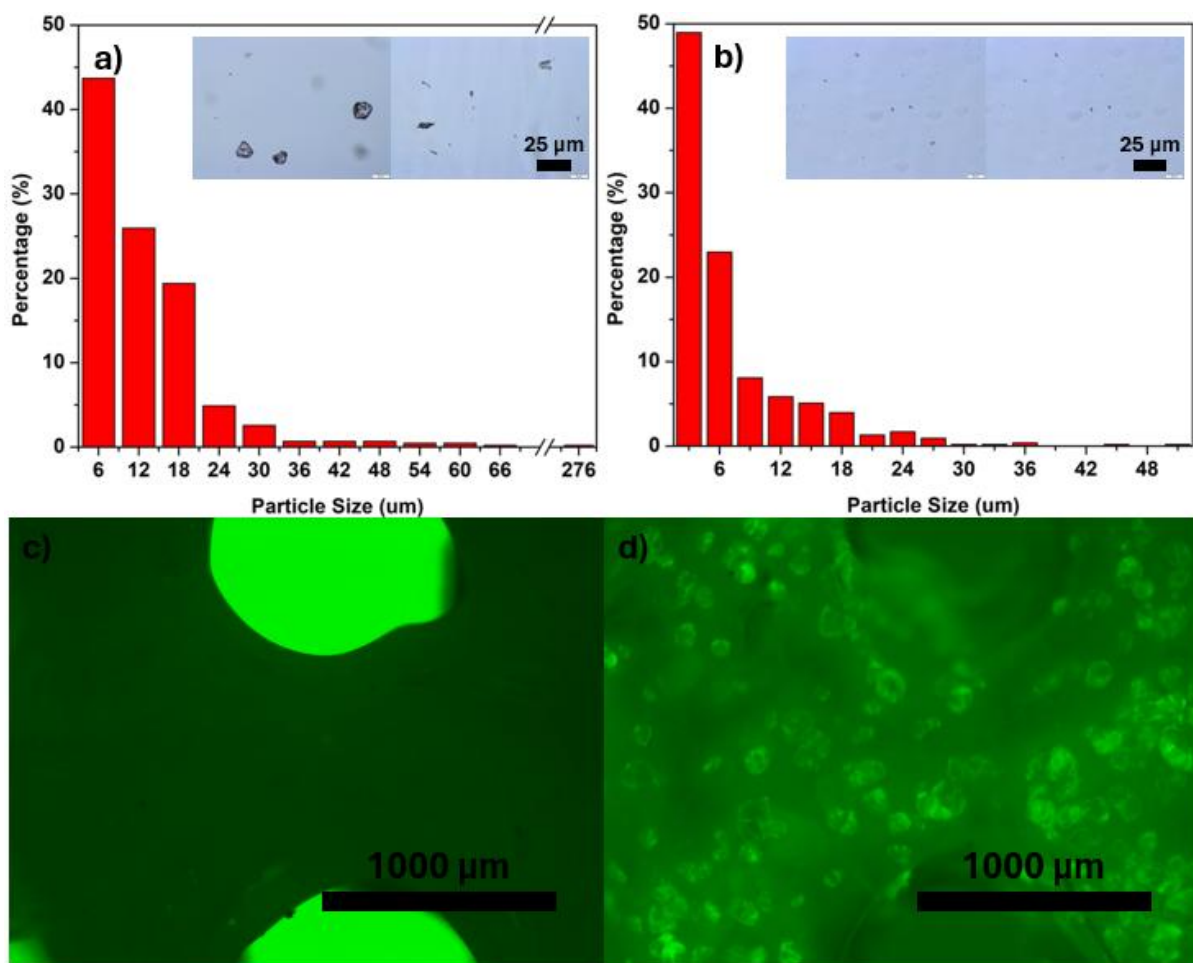


Figure 4.10. Particle size distributions of the microplastic wastewater (a) before filtration and (b) after filtration; Fluorescence microscopy of an etched, P2EHA-coated filter (a) before filtration and (b) after filtration.

4.4 Conclusions

In this study, the impact of incorporating sacrificial PEG with PLA FDM feedstock on processability and mechanical properties were investigated. The sacrificial PEG was subsequently removed via hot water etching to create micro and nano-sized pores on the printed surface. This technology was then applied to the creation of 3-D printed, gravity-driven water filtration columns for microplastic capture. The increase in surface porosity greatly improved the capturing capability of the 3D-printed filters. To further bolster the removal efficiency of the designed system, two different pressure sensitive adhesives, polydopamine (PDA) and poly (2-ethylhexyl acrylate) (P2EHA), were deposited on the surface of the filters to aid with physical microplastic interactions. Both adhesives further increased microplastic capture, but the P2EHA-coated filters outperformed the PDA-coated filters. Finally, the impact of adding more filter layers to the filtration column was examined to assess the upper limit of filtration that could be reached. 20 layers of the etched, P2EHA-coated PLA filters successfully removed 90% of microplastics, successfully demonstrating the application of a simple filtration system for high efficiency microplastic removal that requires only gravity as a driving force. Future work should examine the reusability and total capturing capabilities of this system, as well as its performance on higher fidelity microplastic systems such as laundry effluent where it could be used in practice.

Chapter 5 – Concluding remarks and future works

The continued improvement of methods for water treatment and pollutant removal requires broadening your vision to explore new techniques that can address shortcomings in preexisting systems. The versatility of polymers makes them primed to aid in these advancements, as they possess a large variety of different useful properties and can be processed in innumerable ways for a given application. To help break down the barrier of polymer-based filtration systems, this thesis investigated two different filtration systems, and their conclusions from previous chapters are summarized as follows:

- 1) **SEBS meltblown nonwovens for oil-water separation:** Insight was provided into the fabrication of pure SEBS melt blown nonwovens which previously had been scarcely studied. SEBS tri-block thermoplastic elastomer was successfully processed into fine continuous microfibers for the creation of a nonwoven fabric using a custom lab-scale melt-blowing extrusion process. It was found that SEBS reacts differently when exposed to different types of oils, displaying different levels of interaction and final material consistencies. Mineral oil and crude oil dissolved well the ethylene-butylene midblock, leading to thick, viscous gels, while vegetable-based diester fluids displayed much weaker interactions leading to the nonwovens retaining their elastomeric nature. Gasoline and diesel fuel were incompatible with the fabricated systems due to their benzene content which fully solubilized the styrene endblocks, destroying the gelation capturing mechanism. The demonstrated gel formation phenomenon allowed for exceptional oil-water selectivity and oil capture compared to PP adsorption-based

systems. Ultimately, the synthesized SEBS nonwovens exhibited excellent oil selectivity that show its use in oil spill remediation and immobilization.

- 2) Highly modified PLA filters for microplastic capture:** The impact of sacrificial PEG incorporation into a PLA FDM system was examined for its thermal, rheological, and mechanical changes. The sacrificial PEG was then removed with a hot water etching technique to leave behind micro and nano-sized pore on the printed PLA surface. The created pores were tested for their ability to improve the microplastic removal efficiency of 3D-printed, flow-through filtration columns. The increase in surface area and surface porosity greatly improved the capturing capability of the filters. The deposition of PDA and P2EHA PSAs was then undertaken to improve the physical interactions between the filter surface and the microplastics. Both adhesives provided improvement to the filtration column's removal efficiency, with P2EHA slightly outperforming PDA. Finally, using the etched, P2EHA-coated system, the effect of increasing the number of filter layers in the column was examined from 8-20 layers. The 20-layer tall filtration column was capable of 90% microplastic removal efficiency, successfully demonstrating the system's ability to achieve high efficiency microplastic removal.

To conclude, this chapter will also address the challenges associated with the presented water filtration systems. Although both technologies demonstrated promise for high-efficiency water pollutant removal, there is still significant room for improvement and exploration. Chemical reclamation of the SEBS fibers after oil absorption for reuse, reusability of P2EHA-coated

filters before experiencing a drop in performance, removal of microplastics and/or the P2EHA adhesive from the PLA filters for continued usage, testing on real-world samples such as laundry effluent, and examining the removal of other suspended pollutants using the designed filtration system could all be areas for continued exploration branching from this work.

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