

Fabrication of Porous Biopolymer/ Metal-Organic Framework Composite Membranes for Filtration Applications

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Abstract

Due to the exponential growth of the population and industrialisation over the past decades, the demand for sustainable separations and purification technologies has rapidly increased. Membrane-based separation is one of the most promising techniques since the costs involved is significantly reduced relative to conventional technologies such as distillation which relies on energy-intensive phase changes. However, fabricating sustainable and cost-effective membranes with high separation performance and chemical/thermal stability is still a challenge. Nowadays, biopolymers derived from bio-sources have been attracting significant interest as a result of their biodegradable, recyclable and compostable nature. Poly(lactic acid) (PLA), the second most produced biopolymer, was selected for the fabrication of flat sheet porous membranes in this study. Although PLA is cheaper than other biopolymers, it is relatively soft and has a low modulus and thus additives can be used to stiffen the structure. In this work, the influence of incorporating metal-organic framework (MOF) particles into a PLA matrix was explored through the fabrication of PLA/MOF mixed matrix membranes (MMMs) with the aim of improving mechanical and separation performance i.e. selectivity. The essential novelty of this research is in the fabrication of biodegradable and sustainable flat sheet porous PLA films by the phase inversion method-immersion precipitation technique. In addition, PLA/MOFs mixed matrix porous films are being made for the first time in order to incorporate various types of MOFs into the PLA phase by using the same fabrication technique that produces porous membranes. The effect of fabrication conditions such as the initial crystallinity and concentration of PLA, the type of a non-solvent bath, drying conditions and casting thickness was first explored for pure PLA membranes. Scanning electron microscope (SEM) images showed that membranes had an asymmetric skinned layer which is supported by a thicker porous structure. After some experiments, the polymer concentration was settled at 10 wt% PLA in dimethyl sulfoxide (DMSO) solvent. Pure PLA membranes with a 50 μm casting thickness exhibited a homogeneous structure without shrinkage or excessive brittleness. After establishing viable fabrication conditions for pure PLA membranes,

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PLA/MOF MMMs were then fabricated using established MOFs HKUST-1 and MIL-53. The presence of HKUST-1 and MIL-53 crystals in the PLA matrix was confirmed using X-ray diffractometry (XRD). During the preparation of 5 wt% HKUST-1 loaded PLA/HKUST-1 MMMs, the influence of casting thickness, immersion time and temperature were investigated. Results demonstrated that for PLA/HKUST-1 MMMs cast with a thickness of 50 μm and immersed for 90 minutes at 25 $^{\circ}\text{C}$ was adequate to obtain a homogeneous structure. The influence of increasing HKUST-1 loading, up to 40 wt%, into PLA matrix was also considered. The PLA/HKUST-1 MMMs were successfully fabricated for 5, 10 and 20 wt% HKUST-1 loading. Membrane porosity was increased slightly as HKUST-1 loading increased. However, PLA/HKUST-1 MMMs became increasingly brittle beyond 5 wt% loading which was observed via a tensile strength test. Mechanical and degradation tests were performed to examine the membrane durability. Pure PLA and PLA/HKUST-1 membranes exhibited a tensile strength of $\sim 1\text{--}1.5$ MPa and $\sim 0.5\text{--}1$ MPa, respectively. This suggests that the inclusion of HKUST-1 did not improve the stiffness. Degradation studies showed that pure PLA membranes were capable of withstanding temperature conditions of 50 $^{\circ}\text{C}$ in a water environment for approximately two months, estimated as equivalent to ~ 2 years at 25 $^{\circ}\text{C}$, before any significant loss in mechanical strength could be observed. Pure water successfully passed through all PLA membranes, with flux recorded as high as $1000\text{ l m}^{-2}\text{ h}^{-1}$ at 6 bar feed pressure for a porous membrane of 700 microns in thickness. Membrane microstructure, overall thickness, porosity and the applied pressure influenced water flux. Membrane separation performance was also examined using a number of micron-size particles including corn flour, cement, milk powder, dye and ground coffee. For corn flour particles, pure PLA and 5-20 wt% HKUST-1 loaded PLA/HKUST-1 membranes with $\sim 288\text{--}348\text{ }\mu\text{m}$ thickness, exhibited particle rejections of more than 90%.

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A	Effective film's area
A _C	Cross-sectional area
A _f	Membrane effective area
BDC	1,4-benzenedicarboxylic acid
BSA	Bovine serum albumin
CA	Cellulose acetate
C _f	Concentration of particle compound in the feed
C _p	Concentration of the particle compound in permeate
DMSO	Dimethyl sulfoxide
DSC	Differential scanning calorimetry
E	Young's modulus
F	Applied force
GPC	Gel permeation chromatography
H _m	Heat enthalpy of melting
H _c	heat enthalpy of crystallisation
L	Length of the specimen after testing
L ₀	Original length of the specimen
M	Mass
MeOH	Methanol
MF	Microfiltration
MMMs	Mixed matrix membranes
M _n	Number average molecular weight
MOFs	Metal-organic frameworks

List of Glossary

M _p	Mass of polymer
M _w	Weight average molecular weight
MWCO	Molecular weight cut-off
NF	Nanofiltration
PA	Polyamide
PAN	Polyacrylonitrile
PANI	Polyaniline
PDI	Polydispersity index
PDLA	Poly(D-lactic)
PDLLA	Poly(D,L-lactic acid)
PES	Polyethersulfone
PLA	Poly(lactic acid)
PLLA	Poly(L-lactic)
PP	Polypropylene
PSf	Polysulfone
PTFE	Polytetrafluoroethylene
PVA	Polyvinyl alcohol
PVDF	Polyvinylidene fluorid
PWF	Pure water flux
RO	Reverse osmosis
SDS	Sodium dodecyl sulfate
SEM	Scanning electron microscopy
T _c	Crystallisation temperature
T _d	Degradation temperature at 50% weight loss

List of Glossary

TFC	Thin film composite
TFN	Thin film nanocomposite
T _g	Glass transition temperature
TGA	Thermogravimetric analysis
Th	Film's thickness
THF	Tetrahydrofuran
T _m	Melting temperature
UF	Ultrafiltration
V	Effective film's volume
V _{cp}	Collected permeate volume
V _p	Volume of polymer
V _v	Volume of film's pores 'voids'
XRD	X-ray diffraction
δ _d	Dispersion force component
δ _h	Hydrogen bonding component
δ _p	Polar force component
ε	Strain
σ	Stress
ρ	Density
Φ	Porosity
ρ _p	Density of polymer
χ _{DSC}	Degree of crystallinity

Chapter 1: Introduction

1.1 Research motivation

Water and air are the two essential needs for all living creatures including humans, animals and plants. Unfortunately, nowadays both water and air are mainly polluted due to carbon emissions and other contaminants that are either derived directly or indirectly from petroleum and its derivatives (Elosta, 2016, Kjellstrom *et al.*, 2006, Akpor *et al.*, 2014). Therefore, effective practical solutions must be constructed to overcome or at least reduce the harmful effects of global warming. One suggested solution is to establish/design a sustainable process that can treat polluted water and in the same time be environmentally friendly without causing air pollution. This thesis will explore the manufacturing of novel biopolymer-based porous composite membranes for water purification applications, to contribute towards a sustainable planet.

Due to the continuous growth of the population, the demand for clean water has increased proportionally. Currently, the availability of safe and drinkable water is limited as there are some countries that have no access to safe water. In addition, water scarcity is expected to increase due to the exponential growth of the population. Nearly 70% of the world is covered with water. About 97.5% of the Earth's water is saltwater (oceans) and the other 2.5% being freshwater (Roy and Ragunath, 2018). Even then, only ~1% of the freshwater is easily accessible, while the rest of the freshwater is found in glaciers and snowfields, and is difficult to access i.e. groundwater (Daniel G. Drouin, 2019). In principle, only ~0.007% of the total Earth's water is directly available for human use (Roy and Ragunath, 2018, National Geographic, n.d). The percentage distribution of the Earth's saltwater and freshwater is illustrated in Figure 1.1.

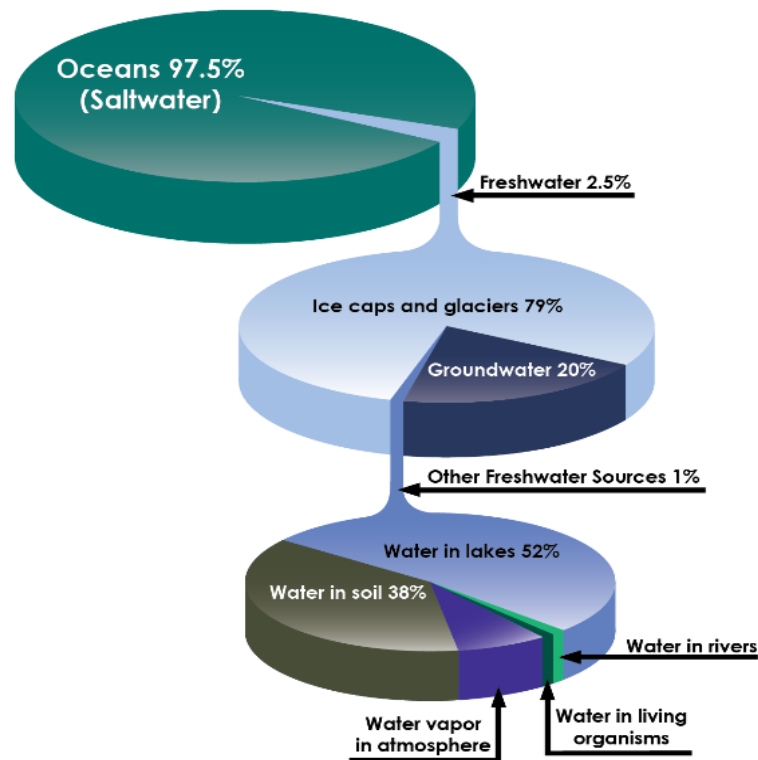


Figure 1.1:The Earth's saltwater and freshwater distribution percentages (NASA, n.d).

United Nations Sustainable Development Goals (2019) and the World Health Organization (WHO) (2019) have reported some statistical data in regards to global water demand and scarcity. In 2017, around 5.3 billion people, 71% of total population, used safely managed drinking-water service that is readily-available when needed (World Health Organization, 2019). In addition, around 6.8 billion people, ~90% of total population, used at least a basic service that is comprised of a required round trip of within 30 minutes to collect drinkable water (World Health Organization, 2019). Moreover, about 785 million people have a lack of access to even basic drinking-water services, including 144 million people that are dependent on surface water. Worldwide, there are more than 2 billion people are using sources of drinking water contaminated with faeces. Contaminated water is very dangerous as it might cause some diseases such as diarrhoea, typhoid, cholera, polio and dysentery and also death. It is estimated that the contaminated drinking water causes around 485,000 deaths every year (World

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Health Organization, 2019). It is expected that by 2025 around half of the global population might live in water-stressed areas. According to the United Nations Sustainable Development Goals (2019), countries registered as high water stress with serious water difficulties in accessing safe and drinkable water are mainly located in north Africa as well as west, central and south Asia. Boretti and Rosa (2019) reported that the scarcity of clean and safe water is a major issue in today's world which might worsen by 2050 due to the increase in global population that is expected to reach 9.4 to 10.2 billion people with an increase of ~22 to 34% as compared to ~7.7 billion. More significantly, it is estimated that by 2050 approximately 6 billion people may suffer from clean water scarcity due to three main reasons which include the increase of water population, increase in demand for water and reduction of water resources. From this, the significance in regards to the scarcity of clean and drinkable water, especially in the future, is clearly understood and therefore requires serious practical solutions.

Among various separation processes, membrane technology is one of the most commercial, promising and cost-effective separation processes that is applicable in a wide range of conditions and applications (Yang *et al.*, 2019b). One of the key drivers of membrane technology is that it has the capability to reduce the energy consumption by ~50% as compared to other process such as evaporation units (Drioli *et al.*, 2017). In addition, replacing other conventional technologies such as evaporation units by membrane technology can reduce the operating cost by more than 75% (Jevons and Awe, 2010). Membrane technology can be used for the removal of micro-sized contaminants such as suspended solids as well as bacteria and viruses. It can also be used to purify water from nano-sized particles such as ions, i.e. salt in seawater desalination for reverse osmosis membranes (Aliku, 2017). The membrane market for water and wastewater treatment as well as industrial processing has been growing

rapidly especially in the last few years. In 2019, the estimated membrane market is 5.4 billion US dollars (Markets and Markets, 2020). This number is projected to reach 8.3 billion US dollars by 2024. The major reasons behind the increase in the membrane market are the growth of the population and the rapid increase in industrialization (Markets and Markets, 2020, Eyvaz and Yüksel, 2018). In addition, other motivators for the membrane market are the raise in awareness in regards to the reuse of wastewater, changes from chemical treatments to physical treatments of water, strict regulations for the treatment and discharge of water, and environmental concerns (Farabegoli *et al.*, 2018, Adewumi and Oguntuase, 2016, Markets and Markets, 2020).

Most commercial membranes materials are petroleum-based such as polyvinylidene fluoride (PVDF), polypropylene (PP), polyacrylonitrile (PAN), polytetrafluoroethylene (PTFE), polyethersulfone (PES), polysulfone (PSf) and polyamide (PA) (Mohanty and Purkait, 2011, Liao *et al.*, 2018). However, these petroleum-based membranes are non-renewable, harms humans and living organisms and pollutes air and water sources (Elosta, 2016, Weber *et al.*, 2002). Most of the existing commercial membranes are derived from petroleum materials. Therefore, replacement of petroleum-derived materials using environment-friendly materials is essential in order to safe the environment and limits the global warming i.e. via producing biodegradable and sustainable membranes. Essentially, the concept of sustainability is to manufacture products through economical processes that reduce the negative environmental impacts while also saving energy and natural resources (United States Environmental Protection Agency, 2017). Moreover, sustainable manufacturing enhances the welfare of the community as well as employees while also ensuring product safety. The approach of sustainable manufacturing reduces energy use, water use, emission and waste generation (Kishawy *et al.*, 2018, Cai *et al.*, 2019). To achieve the concept of sustainable

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manufacturing, the integration of sustainable activities at all levels of manufacturing which includes product, process and system should be applied (Posinasetti, 2018). In addition, this can be further expanded in the re-use, redesign, recycle, remanufacturing, repurposing and refuse of existing processes/products to accomplish the characteristics and objectives of sustainable manufacturing.

Polylactic acid (PLA) is one of the most popular and leading commercial biopolymers that has been recently used in various sectors such as the medical field, packaging, separation and films (Singhvi *et al.*, 2019, Butbunchu and Pathom-Aree, 2019, Lopes *et al.*, 2012). PLA is an eco-friendly bio-based polymer with biodegradable and compostable characteristics (Song *et al.*, 2009, Garrison *et al.*, 2016). In this thesis the potential of manufacturing environment-friendly, sustainable and biodegradable porous PLA membranes for liquid separation will be explored. The study will determine the optimum fabrication conditions of porous flat PLA membrane sheets for water purification by using commercial phase inversion via immersion precipitation technique.

In addition, the study was extended to explore the potential of manufacturing PLA-based composite membranes. Metal-organic frameworks (MOFs) are a class of hybrid ‘organic-inorganic’ materials which basically consists of metal ions or clusters connected by organic linkers/ligands (Chen *et al.*, 2014, Tong *et al.*, 2013). In general, MOFs are very promising in various applications including separation due to their high porosity, high crystallinity and their capabilities to be produced with regular sizes and repeated patterns of pores (Zhang *et al.*, 2013, Campbell *et al.*, 2014). Therefore, to gain the advantage of MOFs, PLA based/MOF composite membranes were prepared using composite mixed matrix membranes method (MMMs).

Research Novelty

The key novelty of this research lies in the fabrication of biodegradable, sustainable and eco-friendly flat porous PLA membrane sheets using the phase inversion via immersion precipitation technique which to the best of my knowledge has never before been attempted. In addition, the fabrication of PLA/MOFs MMMs which has previously never been attempted was established in order to incorporate various types of MOFs into the PLA phase by using the same aforementioned fabrication technique that produces porous membranes. From the literature, PLA and PLA/MOFs composites have been previously fabricated using melt compounding (Akindoyo *et al.*, 2017, Khuenkeao *et al.*, 2016, Kathuria *et al.*, 2013). Thus resulting in a structure that was not porous and therefore unsuitable for water purification. The porous structure of pure PLA and PLA/MOF membranes to be used for water purification applications in this study is considered to be the main contribution of this research. MOFs are incorporated in order to improve mechanical strength, thermal stability and the separation properties of membranes as evident in previous literature regarding gas separation applications (Gholami *et al.*, 2017, Nik *et al.*, 2012, Venna *et al.*, 2015). In this study, fabricated novel porous membranes were thoroughly investigated in terms of mechanical, materials and chemical aspects to gain an understanding of the inter-relationship between processing technique, structural characteristics and material properties.

1.2 Aim and objectives of the research

Aim

The aim of this study is to develop efficient, stable and sustainable porous PLA biopolymer-based and PLA/MOFs mixed matrix composite membranes for water purification that can be used under a wide-range of processing conditions.

Objectives

- Establish preparation methodologies to fabricate chemically/mechanically stable flat sheet asymmetric porous biopolymer (PLA) membranes using the phase inversion *via* immersion precipitation technique.
- Determine the methodologies/parameters for the incorporation of metal organic framework materials into PLA matrix to form asymmetric porous mixed matrix membranes.
- Examine the durability of successful fabricated pure PLA and PLA/MOFs membranes by examining their mechanical and degradation stabilities.
- Evaluate membrane efficiency and the performance of the most optimised and selected pure PLA and PLA/MOFs membranes for water purification (i.e. pure water flux and micro-particle separations).

1.3 Thesis outline

Chapter One has shown the motivations and novelty of research in addition to the aim and objectives as well as the overall overview of the thesis.

Chapter Two will cover an overview on current available separation processes with a comprehensive literature review on membrane technology and its classifications and fabrication techniques. Furthermore, this chapter will address biopolymers and their potential applications with a focus on PLAs. Inorganic and hybrid materials with a focus on MOFs will also be addressed. Furthermore, this chapter will concentrate on composite materials, more specifically MMMs. Up to date research on membrane technology for water purification application will also be broadly addressed.

Chapter Three will present the materials as well as the preparation procedures and techniques used for the fabrication of PLA and PLA/MOFs membranes. In addition,

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material characterisation including SEM, DSC, XRD, TGA and GPC along with their analysis of obtained data will be explained and discussed. Detailed conducted durability experiments including mechanical and degradation stability tests using tensile test along with their calculations will be shown and clarified. Water flux and separation performance experiments will be assessed using Koch membrane system. Density, thickness and porosity of membranes will be measured and their calculation procedure will be shown.

Chapter Four will establish film casting conditions and parameters for the fabrication of novel pure flat sheet asymmetric porous PLA films using the phase inversion *via* immersion precipitation technique. Different initial types/conditions of PLA pellets will be presented and discussed. Furthermore, the fabrication of PLA membranes will be studied in depth and considered through investigations involving various preparation conditions and parameters. In addition, the micro-morphological structure, thermal properties and chemical stability will also be investigated.

Chapter Five will establish the preparation conditions and parameters for the fabrication of PLA/MOFs mixed matrix composite asymmetric porous films using the phase inversion *via* immersion precipitation technique. This chapter will mainly focus on PLA/HKUST-1 MMMs, with a brief investigation on PLA/MIL-53 MMMs. The potential/possibility incorporation of MOFs into PLA matrix will be examined. Moreover, this chapter will concentrate on the HKUST-1 MOF distribution, loading in the PLA matrix in addition to the micro-morphological structure, thermal properties and stability of fabricated PLA/HKUST-1 MMMs.

Chapter Six will examine the characteristic properties of novel PLA and PLA/MOFs membranes. Mechanical properties i.e. stress, strain at peak stress, elastic modulus and

Chapter 1: Introduction

toughness will be measured and reported. Degradation stability of the novel fabricated PLA membranes will be studied and their suggested practical environmental conditions will be clarified. Pure water flux and separation performance of PLA and PLA/HKUST-1 membranes will be measured and their potential practical application use will be evaluated.

Chapter Seven will draw a conclusion of this project and provide some recommendations for the future work.

Chapter 2: Literature Review

2.1 Overview of the current separation processes

Separation processes are necessary in various industrial applications including chemical, petroleum and material processing (Council, 1999). Basically, separation processes can be defined as the transformation of a mixture of materials into two or more products which differ from each other in composition (King, 2013). Chemical, physical and electrical forces have been used to detach particular elements from a mixture (Sorsamäki *et al.*, 2015). The word separation or ‘unmixing’ refers to the different processes and functions for differing industries. There is a large range of industrial activities that include separation processes such as forest products, metal casting, glass production, water treatments, petroleum and petrochemical, and other industrial sectors (Council, 1999, King, 2013).

Various separation processes have been used in industrial applications. The most traditional and common separation and purification processes that are commercially used in industries are crystallisation, distillation, adsorption, absorption and stripping, extraction, and membrane processes (Council, 1999, Rousseau, 1987, Sorsamäki *et al.*, 2015).

One of the oldest unit operations and separation processes that have been widely used in various industrial applications is crystallisation. Crystallisation involves a physical phase transition process that transforms a liquid solution or gas to a solid form with highly ordered molecular, ionic and atomic crystal structures (Yu and Reutzel-Edens, 2003, Harcum, 2008). The aforementioned process is preferred in many industries due to it being an effective means of separation as the process consumes low energy and only requires low heat for crystallisation compared to other separation processes (Council, 1999). In addition, the advantages of using the crystallisation processes can

be extended further to achieve numerous functions such as solidification, crystal production, concentration, purification and separation (Council, 1999, de Haan, 2015).

Distillation is a process that is used to convert liquid or solids into vapour by heating before subsequent condensation into different liquid fractions (Ruan *et al.*, 2019). Basically, the mechanism for separation in regards to distillation occurs based on differences in boiling points of the mixture (Cseri *et al.*, 2018). The main principle behind the distillation process has been used in a variety of industrial applications including petroleum and petrochemical, food processing and water desalination (Barreto and Coelho, 2015, Van der Bruggen, 2003).

Adsorption processes occur via the transportation of molecules from a bulk fluid i.e. gaseous or liquid to a solid surface (Grande, 2012, Goldberg *et al.*, 2007). Molecules in the fluid mixture are called ‘adsorbates’ while the solid surface that the molecules are transported to are called ‘adsorbents’. The adsorbent has to exhibit a highly porous structure with a high affinity for the adsorbates so that the adsorbates can be efficiently deposited at the solid surface of the adsorbent (Rashed, 2013). This process is usually reversible wherein the process is then called desorption. Basically, the purpose of desorption is to release adsorbates from the surface of the adsorbent (Wilcox *et al.*, 2014, Crawford and Quinn, 2017). Desorption can be achieved by reducing the adsorption driving force or weakening the bonds between the adsorbent and adsorbates (Oura *et al.*, 2003). Instances of achieving desorption is by changing the temperature and pressure of the process or by adding another substance that competitively adsorbs the adsorbate, or possibly a combination of both methods (Cavalcante Jr, 2000).

Unlike adsorption, absorption occurs particularly between fluids. The transportation of one or more components comprised of a gaseous phase to a liquid phase is referred to

Chapter 2: Literature Review

as the absorption process (Seader *et al.*, 1998, Chattopadhyay, 2007). In absorption processes, the gaseous component(s) must be soluble in the liquid phase (Chattopadhyay, 2007). The reverse of this process is called stripping whereby a component comprised of the liquid phase transports and dissolves into gaseous phase (Wankat, 2006).

Extraction is one of the common separation processes that is used to extract a solute from another liquid (Berk, 2018). Extraction happens between two immiscible liquid phases in a process known as solvent extraction or liquid-liquid extraction (Hanson, 2013, Ramaswamy *et al.*, 2013, Koncsag and Barbulescu, 2011). In regards to the above, the selection of the solvent is based on the interfacial tension between the two liquids used in consideration (Council, 1999). Liquid-liquid extraction is mainly used to remove undesirable components to purify the original solvent or to recover a valuable component from the original solution (Towler and Sinnott, 2012).

Membrane technology is one of the separation processes that has been widely implemented in various industrial applications (Sirkar, 1997, Goh *et al.*, 2019). Principally, the membrane is a barrier that selectively allows material(s) to pass through while rejecting others in accordance to their particle size (Demeuse, 2009). The schematic representation of molecular transport through a membrane separation barrier is shown in Figure 2.1. In membrane separation processes, the feed becomes separated into two different phases; the materials that pass through the membrane i.e. the ‘permeate’, and the amount of the feed that is rejected by the membrane i.e. the ‘retentate’ (Strathmann, 1981). The transportation of materials in membrane separation processes is mainly dependent on the operating conditions and the characteristics of the membrane (Porter, 1990, Wan *et al.*, 2010).

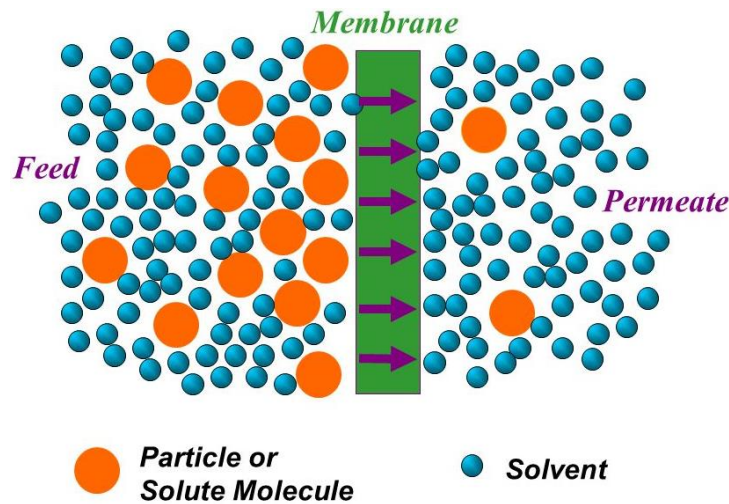


Figure 2.1: Schematic representation of molecular transport through a membrane separation barrier. Adapted from Parhi (2012).

Most of the current separation processes available have been greatly improved. In addition, more than one separation option can be considered to be valuable for most industrial processes. However, the current existing separation processes could be further improved in terms of operational cost, energy consumption, the use/re-use of raw materials and by-products, and separation efficiency quality and sustainability.

2.2 Membrane technology

There are several advantages to using membranes in a separation process as there are no phase changes involved during the separation thus requiring less energy in comparison to conventional separation processes such as distillation and adsorption (Mishra *et al.*, 2009). In addition, operations involved in membrane processes are simple and can be integrated into other units for applications in catalytic reactors, distillation, water treatment and desalination (Dixon, 1999, Drioli and Romano, 2001). In terms of the environment, there is a potential for more rational use of raw materials and reuse of by-products (Buonomenna, 2016). Membrane processes can be used for both gas and liquid separations. Examples of gas separation processes are carbon capture, natural gas purification and air separation (Ji and Zhao, 2017, Ulbricht, 2006). Kidney blood

detoxification, sterile filtration, oil/water separation, water treatment and desalination are some applications of liquid membrane separation processes (Ulbricht, 2014, Lass, 2017).

Implementing a membrane is a physical separation process which does not involve phase changes and utilises no chemical additives to instigate separation (Macedonio and Drioli, 2017). With this, a driving force(s) is required for membrane separation processes to occur. The driving force could include pressure difference, concentration gradient, temperature and electrical field (Probstein *et al.*, 1983, Nath, 2017).

Membranes barrier structures classified mainly into porous and non-porous (Buonomenna, 2016). For porous membrane, viscous flow and size exclusion/ or sieving are main parameters that effect on/ control selectivity and transport rate (Ulbricht, 2006); (Jia and Wu, 2016). Where in non-porous membrane, interactions between membrane material and permeant are main parameters that effect on/ control selectivity and transport rate (Ulbricht, 2006). Diffusion/ solution model describe the transport mechanism, and the separation selectivity between two compounds can be determined by the solution/ or diffusion selectivity (Tyona, 2013).

It is important to note that the selectivity and permeability of membrane are totally controlled by membrane fouling or concentration polarization (Ulbricht, 2006). Concentration polarization occur because of the concentration enhancement of rejected species on the membrane surface as function of transmembrane flow (Ulbricht, 2006). Fouling considered the main challenge of membrane process, and it occur due to unwanted adsorption or deposition of matter on the membrane separation layer (Ulbricht, 2006).

2.3 Membrane fabrication techniques

There are several techniques that have been used to prepare polymeric, inorganic and composite membranes. The selection of technique for the fabrication of membranes mainly depends on the type of materials and the desired membrane structure and shape (Duarte and Bordado, 2016). Considering the membrane structure, the final produced membrane microstructure defined in terms of density or porosity is essentially based on the selected fabrication technique (Thomas *et al.*, 2017b, Cuperus and Smolders, 1991). In addition, each technique has its own advantage and disadvantage i.e. preparation/fabrication challenges and operational limitations (Low *et al.*, 2017). The most common preparation techniques used for the fabrication of polymeric membranes are interfacial polymerisation, phase inversion, electrospinning, track-etching, sintering and stretching (Tan and Rodrigue, 2019, Lee *et al.*, 2016). Interfacial polymerisation, phase inversion, spin coating, dip coating, multilayer polyelectrolyte deposition, dual layer co-extrusion/co-casting and grafting are some of the most common and developed techniques used for the fabrication of composite membranes (Buonomenna, 2016, Duarte and Bordado, 2016, Liu *et al.*, 2020).

Phase inversion is the most common technique for the fabrication of membranes in liquid and gas separation applications (Lu and Chung, 2019). Phase inversion can be further classified into different sub-methods such as precipitation by solvent evaporation, precipitation from the vapour phase, precipitation by controlled evaporation, thermal precipitation and immersion precipitation (Guillen *et al.*, 2011). Precipitation by solvent evaporation gives a nonporous ‘dense’ membrane while a porous membrane without a top dense layer can be produced via the precipitation from the vapour phase method (Mulder, 1991). Asymmetric skinned membranes with a porous bottom region and a top dense layer can be produced using precipitation by

controlled evaporation, thermal precipitation and immersion precipitation methods (Mulder, 1991). Schematic representations of various membrane morphologies are illustrated in Figure 2.2.

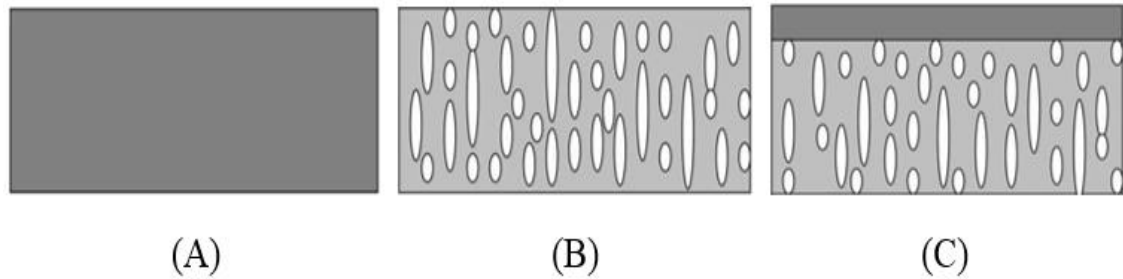


Figure 2.2: Schematic representation of various membrane morphologies. (A): dense membrane structure, (B): porous membrane structure, and (C): asymmetric membrane structure. Adapted from Sridhar *et al.* (2007).

Phase inversion by immersion precipitation is the most common, simple, successful, well-understood and commercial technique that produces asymmetric skinned membranes suitable for liquid filtration i.e. water (Suwaileh *et al.*, 2018, Mulder, 1991, Yu *et al.*, 2014). This technique involves dissolving a polymer in a suitable solvent and casting the resulting solution in a nonwoven substrate before immediate immersion in a nonsolvent bath i.e. water. Phase exchange occurs as the solvent diffuses into the nonsolvent bath and the nonsolvent diffuses into the casted film (Ge *et al.*, 2013, Hilal *et al.*, 2015). Proceeding the solvent and nonsolvent exchange process, a solid film with an asymmetric structure is thus obtained (De Zarate *et al.*, 1995, Purkait *et al.*, 2018). A schematic drawing representation of the preparation of flat sheet membranes using phase inversion by immersion precipitation technique is shown in Figure 2.3.

The structure of the membrane can be modified depending on different interdependent factors that have a major effect on the final membrane morphology (Bindal *et al.*, 1996, Mulder, 2013). By varying one or more of these factors/parameters, the resulting membrane structure can be varied from exhibiting a very open porous structure to a very

non-porous dense structure (Bindal *et al.*, 1996, Mulder, 2013). These factors/parameters are:

- type of polymer
- type of solvent
- type of non-solvent
- composition of the casting solution
- composition of the nonsolvent bath
- gelation and crystallisation behaviour of polymers
- location of the liquid-liquid demixing gap
- temperature of the casting solution
- temperature of the nonsolvent bath
- evaporation time

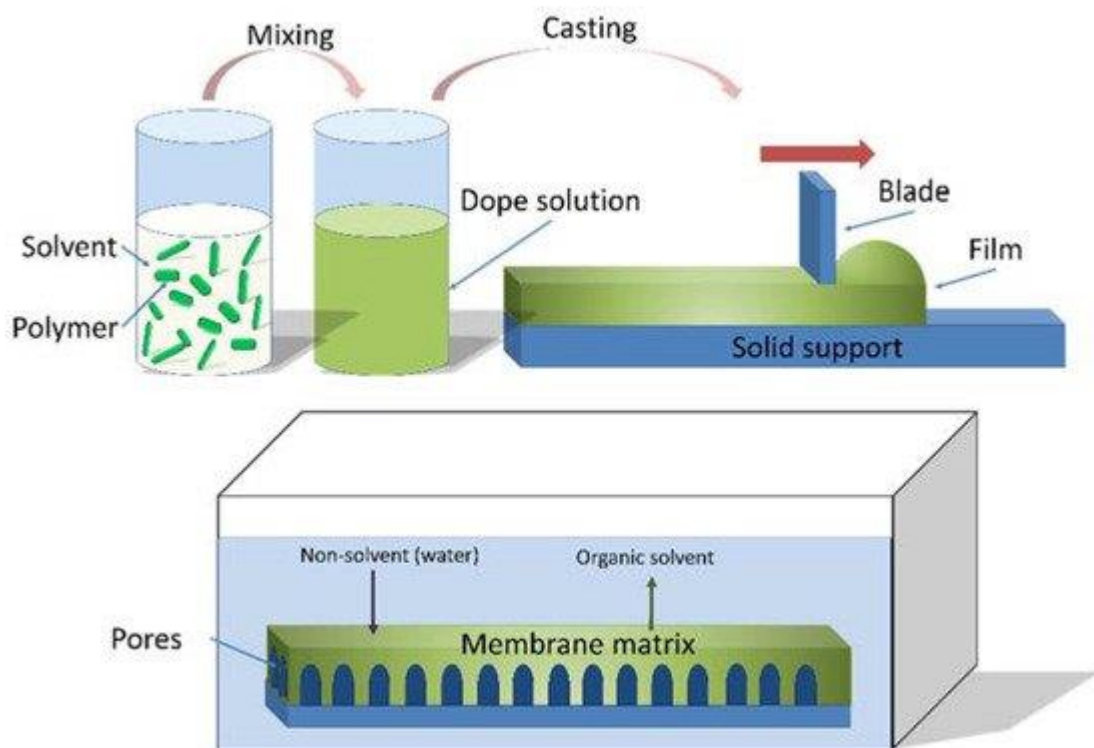


Figure 2.3: Schematic drawing representing the preparation of flat sheet membranes via the phase inversion by immersion precipitation technique (Dong *et al.*, 2018).

2.4 Membrane filtration modes

Membrane filtration is usually operated in two modes: (1) dead-end, or (2) cross flow. In the dead-end mode, both the feed flow and permeate direction are perpendicular to the membrane surface whereas in the cross flow mode, the feed flow is parallel to the membrane surface and only a portion of the feed passes through the membrane surface under driven force (Herterich *et al.*, 2017, Noble and Stern, 1995). This is graphically presented in Figure 2.4.

In both modes the contaminants accumulate on the surface as filtration progresses with time and as a consequence reduces the membrane efficiency (Herterich *et al.*, 2017). In applying feed flow, the dead-end filtration mode produces a stream consisting of a permeate 'filtrate' while the rejected particles accumulate on the membrane surface to form a filter cake. However, the feed produces two streams i.e. the permeate and retentate that contains some solid contaminants in the cross flow mode (Bhave, 1996). A higher flux could be achieved by implementing the cross flow mode as the feed flow continuously moves parallel to the membrane and continuously removes some retained materials. In the dead-end flow filtration mode on the other hand, the solid contaminants build up on the membrane surface resulting in a fast drop in terms of flux (Singh, 2014, Pal, 2017). In terms of operating cost, the dead-end mode is more cost effective since the cross flow mode requires extra amounts of energy to circulate the feed flow (Li, 1972).

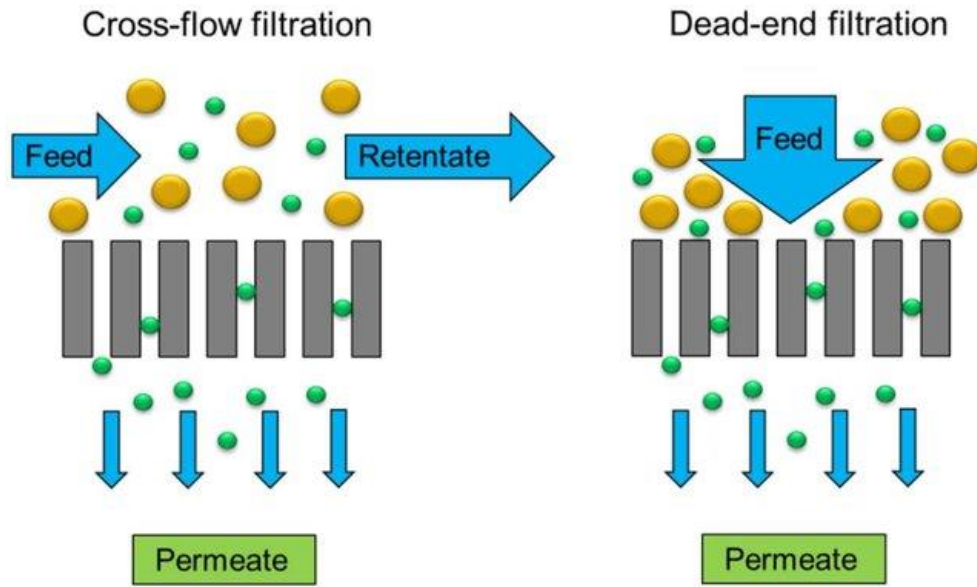


Figure 2.4: Schematic design of dead-end and cross flow modes (Ketola, 2016).

2.5 Membrane classifications

Membranes can be mainly classified with regards to their; (1) material type, (2) morphology, and (3) configuration, as summarised in Table 2.1.

Table 2.1: Membrane classifications in terms of material type, morphological structure, and configuration (Elghaffar and Tieama, 2017, Warsinger et al., 2018).

Configuration	Morphology	Material type
Flat sheet	Symmetric	Organic
Hollow fibres	-porous	-synthetic
Tubular	-dense	-natural
Spiral wound	Asymmetric	Inorganic
	-porous with dense layer	-zeolite
	-composite i.e. MMM	-ceramic
		-carbon based

2.5.1 Membrane configurations

The basic and most common membrane configurations/modules comprise of the flat sheet, hollow fibre, tubular and spiral wound (Bakar and Tan, 2016). The selection in terms of the membrane shape varies depending on its application. Each membrane configuration/module exhibits specific characteristics based on the cost of processing and maintenance, packing density, hold up volume, pressure drop, cleaning procedure and feed quality (Wenten, 2005). Each type of membrane shape has its own limitations and challenges in terms of application, preparations and operations. Schematic designs of various membrane configurations are presented in Figure 2.5.

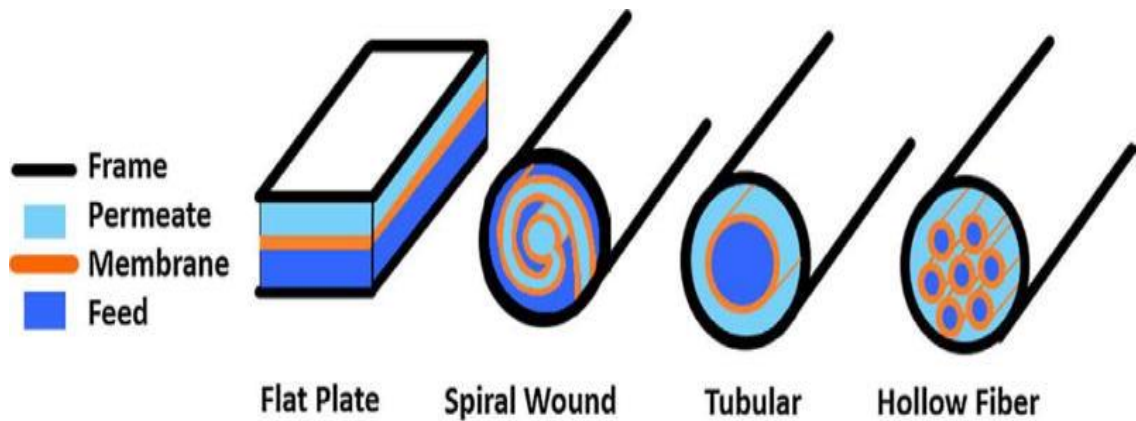


Figure 2.5: Schematic design of various membrane configurations (Warsinger *et al.*, 2018).

Among all the membrane configurations, the tubular module gives the lowest pressure drop and lowest requirements in terms of pre-treatments (Mallevalle *et al.*, 1996). In addition, the tubular membrane configuration has a good fouling resistance (Gude, 2018). Moreover, tubular membranes do not require a support which reduces resistance from the boundary layer (Sun, 2014). Despite the above, the tubular configuration is considerably costly due to its low packing density (Othman *et al.*, 2020). Its low surface area is also considered to be a main disadvantage (Sun, 2014).

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The spiral wound membrane has the advantage of exhibiting a high surface area for filtration units as well as good packing density (Othman *et al.*, 2020, Lu and Chung, 2019). In addition, spiral wound is relatively easy to fabricate and integrate into other processes (Warsinger *et al.*, 2018). In terms of cost, the spiral wound configuration is considered inexpensive compared to other modules (Sun, 2014). Despite this, fouling issues are considered to be the biggest downside of spiral wound membranes which reduces membrane efficiency and membrane lifetime (Warsinger *et al.*, 2018).

A key advantage of hollow fibre membranes are its high packing density which only consumes a small floor space (Bakar and Tan, 2016). In addition, hollow fibre membranes are easy to clean, relatively cost effective and exhibits the highest hold up volume compared to other configurations (Wenten, 2005). However, the poor fouling resistance and high pressure drop are the main drawbacks (Warsinger *et al.*, 2018, Liu *et al.*, 2011, Hernández *et al.*, 2016).

The advantages of flat sheet membranes lies in its ease of fabrication and the low pressure requirement for separation compared to other configurations (Akhondi and Pronk W, 2015). Flat sheet membranes are also highly applicable and considerable in preliminary research studies as they are easy to use, replace, test and clean (Zare and Kargari, 2018, Thomas *et al.*, 2017a). Despite the advantages, Thanh *et al.* (2019) has reported that flat sheet membranes have not been installed at a large industrial scale due to its very low packing density and surface area per volume compared to other configurations. Utilised design of flat sheets used in various industries are referred to as the plate and frame module (Camacho *et al.*, 2013). Basically, the plate and frame module is built-up of multi flat sheets that are placed in free spaces supported by plates and held together by two rectangular frames (Thanh *et al.*, 2019). Using the plate and frame module can increase the effective area of membranes since multiple membranes

can be installed in the same frame (Camacho *et al.*, 2013). Moreover, damaged membranes can be easily removed or replaced in the plate and frame membranes module (Heldman *et al.*, 2018). The general design of the plate and frame membrane is graphically presented in Figure 2.6.

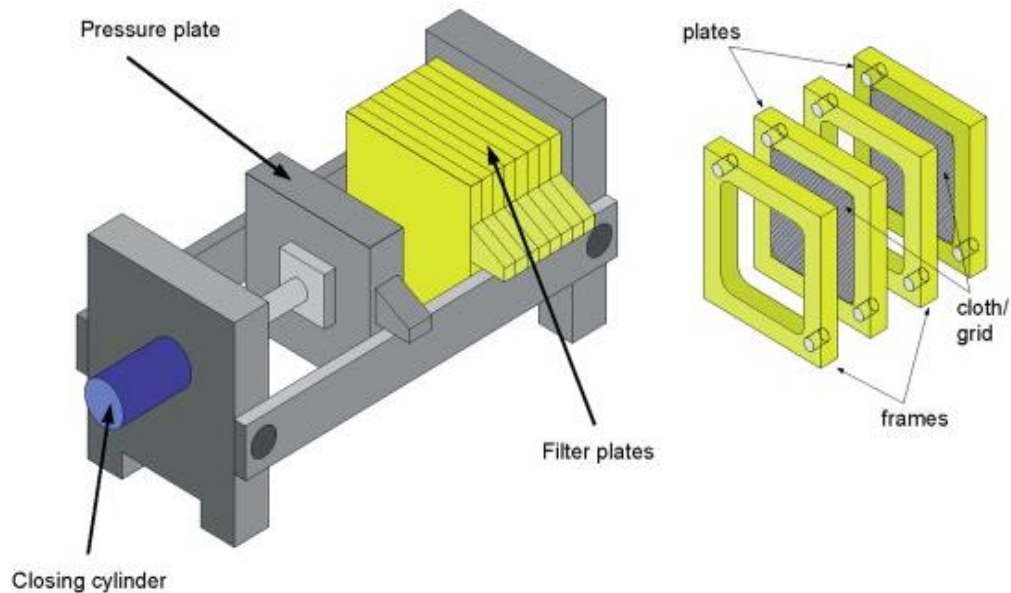


Figure 2.6: General arrangement of plate and frame filter along with the essential elements (Sparks, 2012).

2.5.2 Membrane morphology

Membranes can be mainly categorised into porous and non-porous structures (Bazzarelli *et al.*, 2015). Porous structures are further classified according to their pore diameters i.e. microporous ($< 2\text{nm}$), mesoporous ($2 - 50\text{nm}$) and macroporous ($50 - 500\text{nm}$) (Ulbricht, 2006). Based on pore size, membranes can be classified into four main categories. In the order of large to small pore sizes, they are as follows: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) membranes (Shon *et al.*, 2013). The selection for the type of membrane is mainly dependent on the nature and type of feed, intended application and final purity (Ricceri *et al.*, 2019, Beltrán and Koo-Oshima, 2006). Every type of membrane category has different structural characteristics and uses. The average pore size and pressure requirements of

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membranes used in various liquid separation processes are shown in Figure 2.7. Typically, the MF and UF are porous membranes while NF are porous isotropic or symmetric membranes and UF are porous asymmetric membranes (Worch, 2019). NF has finely porous asymmetric/composite membrane structures. On the other hand, non-porous asymmetric/composite membrane is the typical structure for RO membranes (Pendergast and Hoek, 2011, Sagle and Freeman, 2004).

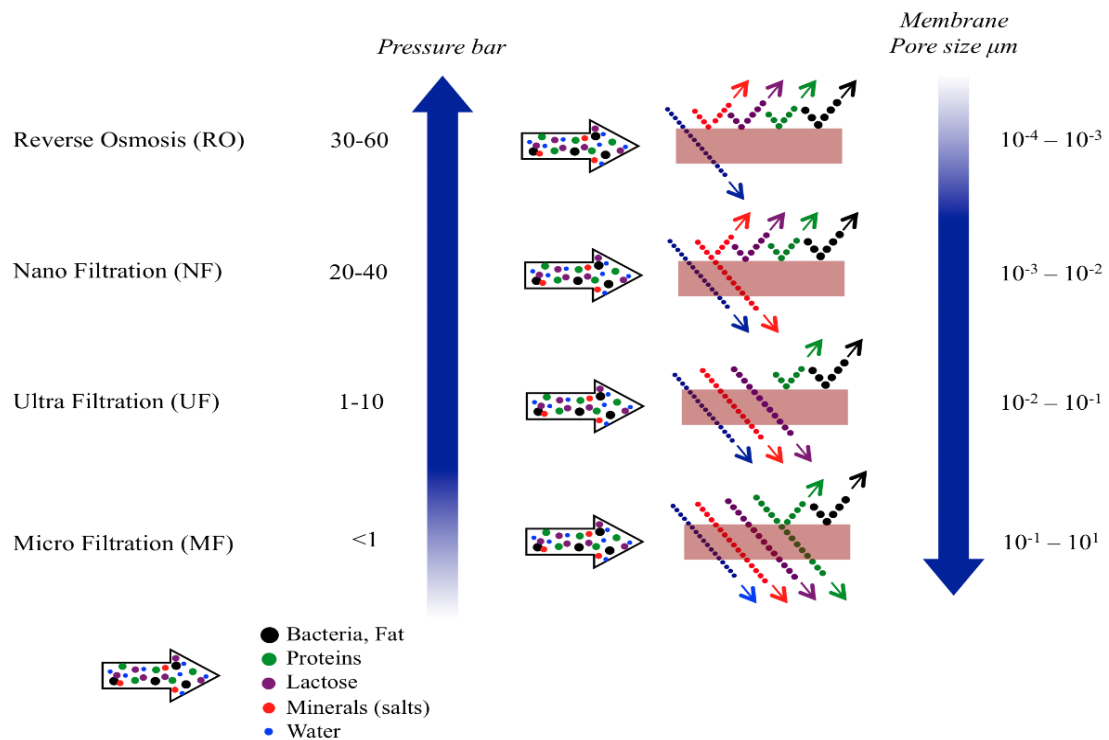


Figure 2.7: Average pore size and pressure requirements of membranes used in various liquid separation processes (Wu and Imai, 2012).

Many studies have reported the key characteristics and features of various membrane separation processes such as MF, UF, NF and RO for liquid filtration i.e. water treatments and purification. Assessing the results for pure water flux/permeability is a very useful approach to explore and oversee the potential of fabricated membranes for implementation in separation processes/applications (Mulyati and Arahman, 2017). The technical aspects involved in the separation process of commercial membranes in regards to their typical pure water flux, applied pressure, pore size and membrane

morphological structure are summarised in Table 2.2. Data in Table 2.2 can be considered as a guide to estimate the relevant separation process of new fabricated membranes i.e. novel membranes in this study, with the commercial membranes reported in available literature.

Table 2.2: Relevant technical aspects for separation processes of commercial membranes. Adapted from (Maddah *et al.*, 2018, Tawalbeh *et al.*, 2018, Buonomenna, 2016, Shon *et al.*, 2013). MF: microfiltration, UF: ultrafiltration, NF: nanofiltration and RO: reverse osmosis.

Separation process	MF	UF	NF	RO
Morphology	Porous (a)symmetric	Porous asymmetric	Finely porous asymmetric/composite	Nonporous asymmetric/composite
Pore size (nm)	100-5000	5-200	1-5	<1
Pressure required (bar)	0.5-5	1-10	5-40	10-100
Typical water flux (L.m⁻².hr⁻¹)	500-10,000	100-2000	20-200	10-100

In terms of membrane structures, there are two classifications; isotropic “symmetric” and anisotropic “asymmetric” membranes as graphically presented in Figure 2.8 (Buonomenna, 2016). Symmetric membranes have only a single layer while asymmetric membranes have two or more layers (Benjamin and Lawler, 2013). Classical asymmetric membranes exhibit a very thin and dense top layer referred to as the “skin layer” or “active layer” while the bottom layer is porous (Lewis, 2018). These layers can be fabricated from either the same type of materials or from different materials. Membranes with layers made up of the same type of materials are referred to as “integrally skinned asymmetric membranes”. On the other hand, membranes with layers

made from different materials type are referred to as “composite membranes” (Duarte and Bordado, 2016). The thickness of symmetric membrane layers approximate about 10 - 200 μm whereas the thickness of the dense and porous layers for asymmetric membranes are in the range of 0.1 - 0.5 μm and 50 - 150 μm , respectively (Mulder, 1991).

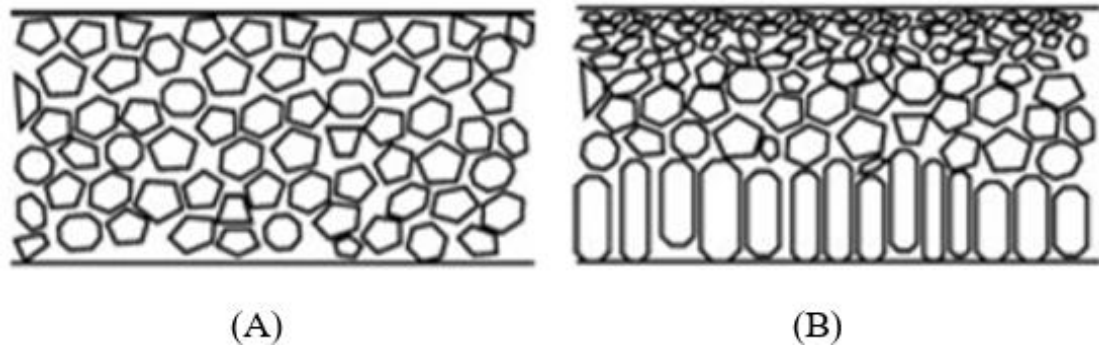


Figure 2.8: Schematic design of (A) symmetric and (B) asymmetric membrane morphologies (Asatekin and Mayes, 2009).

2.5.3 Membrane material type

Up to date, various types of materials have been used for membrane synthesis. Each type of membrane has different characteristics and applications depending on the type of material used for fabrication. Basically, membrane materials are classified in two types; (1) organic, and (2) inorganic (Meynen *et al.*, 2014). General comparisons between organic and inorganic membranes are presented in Table 2.3.

Polymeric membranes are made completely from organic polymers. Examples of these membranes include PVDF, PES, polyvinyl alcohol (PVA), cellulose acetate (CA), PLA and chitosan (Pendergast and Hoek, 2011, Madaeni *et al.*, 2015). Organic polymers have low cost, small footprint and high flexibility (Caro, 2016). Despite the advantages, there are some challenges that limit the use of polymeric membranes such as poor thermal and chemical stabilities and poor mechanical strength (Madaeni *et al.*, 2015, Freger *et al.*, 2005). In addition, issues in regards to fouling, swelling, chemical degradation, low

flux/selectivity and compaction which build up over time cause reductions in membrane efficiency (Souza, 2013).

Another type of membrane is made from inorganic materials such as metals, ceramics, carbon molecular sieves, metal organic frameworks (MOFs) and oxides (Pendergast and Hoek, 2011, Ahmadi *et al.*, 2018). These types of membranes exhibit high mechanical properties, good chemical stability and good thermal stability (Meynenl'p and Buekenhoudt, 2012). In addition, membranes fabricated from inorganic materials have the advantage of producing membranes with uniform molecular pore sizes (Al-Maythalony, 2019). Unlike organic membranes, inorganic membranes do not suffer from issues of swelling (Daramola *et al.*, 2012). Despite this, inorganic membranes are expensive to produce and difficult to fabricate for a large area of applications (Ahmadi *et al.*, 2018, Nunes, 2008). Moreover, they are also more brittle than organic membranes (Daramola *et al.*, 2012). The characteristics of organic and inorganic membranes are summarised in Table 2.2.

Table 2.3: Summary of the comparison between organic and inorganics membranes (Madaeni et al., 2015, Ahmadi et al., 2018, Daramola et al., 2012).

Organic membranes	Inorganic membranes
Chemically unstable	Chemically stable
Thermally unstable	Thermally stable
Less brittle	More brittle
Do swell	Do not swell
Form non-uniform pore sizes	Form uniform pore sizes
Cheap to produce	Expensive to produce
High flexibility	Low flexibility
Poor mechanical properties	High mechanical properties

To overcome the challenges of both organic and inorganic membranes, a new class of membranes i.e. composite membranes have been explored. The main motivation behind exploring composite membranes is to develop and enhance the structure of membranes by combining the advantages and properties of different materials to compose them in a single membrane.

2.6 Composite membranes

Classical composite membranes consist of two or more layers that are made from different type of materials (Khayet and Matsuura, 2011). Usually, the layer that is in contact with the feed side is the thin and dense layer referred to as the active skin layer which is responsible for the membranes separation properties such as selectivity and permeability (Buonomenna, 2016, Duarte and Bordado, 2016). The porous sublayer(s) are mainly responsible in providing the mechanical strength for the membranes to operate under high pressure conditions e.g. as in NF and RO (Yang *et al.*, 2019b). The thickness of the skin layer should be as thin as possible to reduce flow resistance and to provide high separation properties i.e. flux (Ismail and Yean, 2003, Freemantle, 2005).

A new class of composite membranes referred to as “mixed matrix membranes (MMMs)” have been discovered and are increasingly used. MMMs are very promising due to their advantages over other type of membranes as their uniqueness comes from combining the properties of both inorganic and organic materials in one single membrane layer/matrix (Denny *et al.*, 2018, Ahmad *et al.*, 2016b, Jusoh *et al.*, 2016).

Mixed Matrix Membranes (MMMs)

MMMs are considered to be one of the most promising category of membranes that have a high potential to be considered in future applications. MMMs are composed of inorganic materials (or fillers) and organic polymers with no distinct layered

morphology and ideally with inorganic particles being dispersed throughout the whole membrane as shown in Figure 2.9 (Souza, 2013).

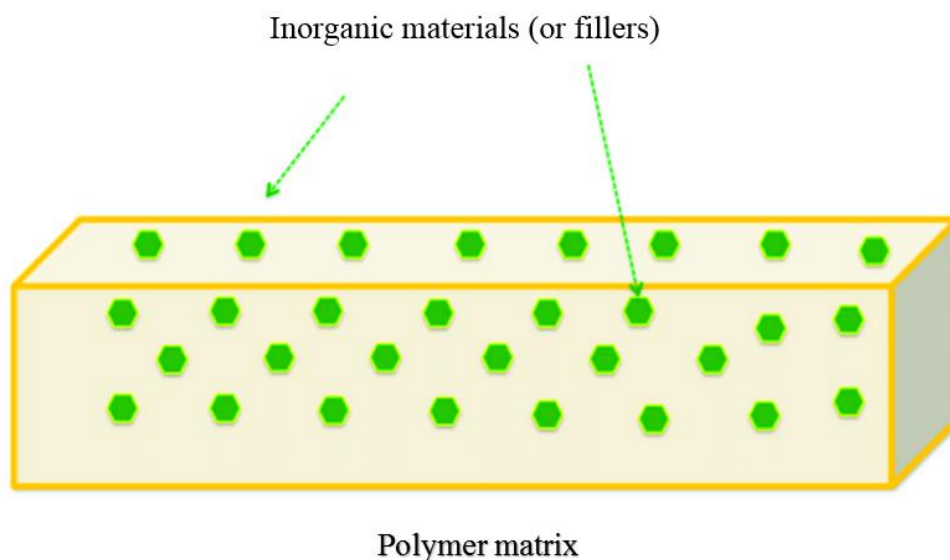


Figure 2.9: Schematic design of an ideal MMM morphology (Castro-Muñoz and Fíla, 2018).

The challenges and limitations of each type of material can be overcome and moderated as a result of combining two or more classes of materials together. In MMMs, a membrane with low manufacturing cost, high mechanical properties, good stability, ease and flexibility in fabrication, high packing density and high separation performance can be achieved (Zimmerman, 1997, Yang *et al.*, 2019b). Typically, inorganic particles such as MOFs, silica and zeolites are added to the polymeric membrane phase/matrix to gain the key characteristics of organic membranes i.e. flexibility, low cost production and high packing density while also inheriting the features of inorganic materials, in particular their superior selectivity (Dong *et al.*, 2013, Meireles *et al.*, 2016). Common techniques in MMM fabrication are phase inversion and sol-gel processes (Pendergast and Hoek, 2011). Dip coating, dispersing crosslinking and interfacial polymerisation are also some techniques used for MMM fabrication (Yang *et al.*, 2019b).

According to Wara (1995), the selectivity increased when particles of ceramic alumina are dispersed in CA membranes through the phase inversion process. Maximous (2009)

demonstrated that the addition of alumina nanoparticles into PES UF membrane has increased flux and reduced fouling. Ebert (2004) reported that inorganic Titania nanoparticle fillers added to PVDF via phase inversion improves membrane stability. Another way of fabricating MMMs are through the addition of organic materials into inorganic matrices. Arkas (2005) fabricated MMMs by adding organosilicon dendritic polymers into a porous ceramic membrane. The resulting synthesised MMM effectively improved in removing some toxic compounds from water. Moreover, improvements in terms of chemical stability and the possibility of filter regeneration were also observed.

There are two main challenges associated with the fabrication of MMM; weak particle-polymer interaction and particle aggregation (Zhang *et al.*, 2016). A common technique to overcome or reduce the issue of aggregation is to disperse the inorganic particles in the solvent until the particles are sufficiently mixed before adding the polymer to the solution (Aroon *et al.*, 2010). The particle-polymer interfacial interaction can be improved by using inorganic-organic hybrid materials such as MOFs due to the existence of their organic linker in their structure which thus characterises them to exhibit higher affinity for polymeric chains and therefore capable of enhancing the adhesion between inorganic-organic hybrid particles and the polymer phase (Elrasheedy *et al.*, 2019). Hence, implementing hybrid materials such as MOFs have a high potential in overcoming the issue of weak particle-polymer interaction and hence improve the adhesion in MMM fabrication (Lin *et al.*, 2014).

2.7 Metal organic frameworks (MOFs)

Unlike organic or inorganic materials, metal-organic frameworks (MOFs) are a hybrid class of porous materials constructed from metal ion- or cluster-containing nodes with organic linkers as graphically presented in Figure 2.10 (Li *et al.*, 1999, Zhou *et al.*, 2012, Safaei *et al.*, 2019). MOFs have been a very attractive and promising class of materials

in various research fields due to their structural and functional flexibility and multi-structural ability (Li *et al.*, 2014, Stock and Biswas, 2012). In addition, MOFs also have a high potential to be used in several applications including catalysts, energy transfer and storage, sensor, drug delivery, fuel cell, biomedical, and separation fields (Yuan *et al.*, 2018, Safaei *et al.*, 2019).

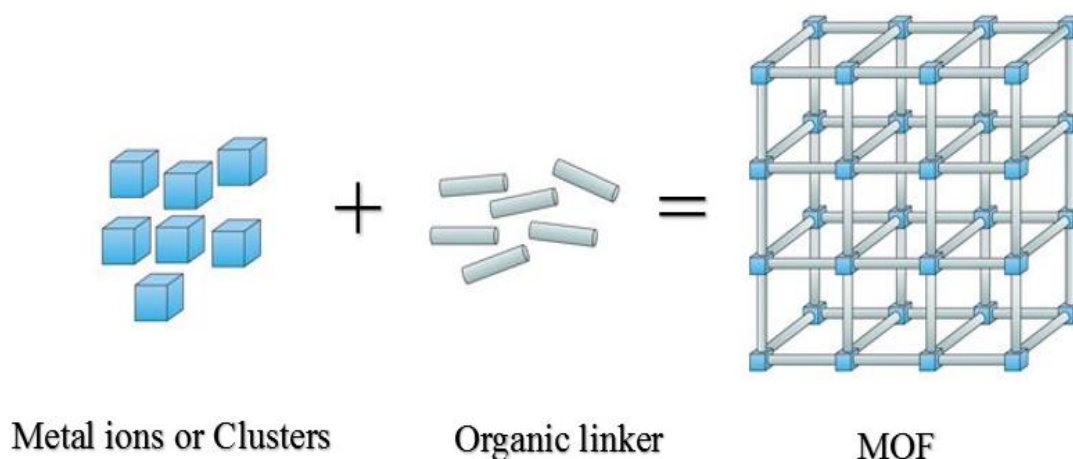


Figure 2.10: Constructed structure of MOF (Sharmin and Zafar, 2016).

The final structure and properties of MOFs depend on the selected primary building blocks with regard to the type of metals and organic ligands (Cook *et al.*, 2013, Aljammal *et al.*, 2019). In addition, parameters such as reaction time, pressure, temperature, concentration, pH and type of solvent have to be considered in MOF synthesis processes (Seetharaj *et al.*, 2019, Cheong and Moh, 2018, Stock and Biswas, 2012). To produce MOFs with specific structures and desired features, a number of synthetic methods can be applied including microwave assisted, heating and ultrasound, hydrothermal ‘solvothermal’, slow diffusion, mechanochemical and electrochemical (Chen *et al.*, 2005, Qiu and Zhu, 2009, Mueller *et al.*, 2006, Pichon *et al.*, 2006, Morsali *et al.*, 2015).

A wide range of MOFs have been produced and developed with numerous advantages to meet certain application requirements (Baumann *et al.*, 2019). Key motivators and

advantages in implementing MOFs are their high surface area, high crystallinity, high porosity, super architecture flexibility, tuneable chemical structure and multifunctional properties i.e. controlling their pore environment and consequently control in their structure and properties (Vikrant *et al.*, 2017, Kareem and Alrubaye, 2019, Zhou *et al.*, 2012). Compared to other inorganic and hybrid materials such as zeolites, MOFs have bigger surface areas of up to $5,900\text{m}^2.\text{g}^{-1}$ (Férey *et al.*, 2005). Along with these advantages, MOFs can offer better compatibility with polymer linkers compared to zeolites (Mahajan *et al.*, 2002).

Nevertheless, some disadvantages such as poor selectivity and low capacity of adsorption in addition to difficulties in regeneration/recycling limit their practical use (Zhang *et al.*, 2019). In addition, MOFs have lower thermal stability compared to zeolites due to their weak coordinate covalent bonds. Moreover, MOFs have higher production costs compared to other porous materials such as zeolite (Thomas-Hillman *et al.*, 2018). Many MOFs have limited applications because they are unstable in water and/or other harsh conditions (Yuan *et al.*, 2018). Operating conditions, organic linker, metal ions/clusters, metal-ligand coordination geometry and pore surface hydrophobicity are the main factors that can influence and control the stability of MOFs (Wang *et al.*, 2016, Canivet *et al.*, 2014, Burtch *et al.*, 2014). Examples of some MOFs with their constructed metal ions/clusters and types of organic ligands along with their BET surface area are presented in Table 2.4.

Table 2.4: Some examples of MOFs.

MOFs	Metal ions or clusters	Organic linkers	BET surface area (m ² .g ⁻¹)	Reference
HKUST-1	[Cu (NO ₃) ₂ · 3H ₂ O]	BTC	1009	(Lin <i>et al.</i> , 2012)
MIL-53(Al)	[Al(OH)(COO) ₂] _n	BDC	1181	(Loiseau <i>et al.</i> , 2004)
MIL-101(Cr)	[Cr ₃ (μ ₃ -O)(COO) ₆]	BDC	4100	(Férey <i>et al.</i> , 2005)
MIL-101(Fe)	[Fe ₃ (μ ₃ -O)(COO) ₆]	BDC	2823	(Lupu <i>et al.</i> , 2011)
NOTT-300	[Al(OH)(COO) ₂] _n	BPTA	1370	(Yang <i>et al.</i> , 2012)
MOF-74(Zn)	[Zn(NO ₃) ₂ · 4H ₂ O]	DHTA	1474	(Adhikari and Lin, 2014)
MOF-74(Cu)	[Cu(NO ₃) ₂ · 2.5H ₂ O]	DHTA	1345	(Adhikari and Lin, 2014)
ZIF-8	[ZnN ₄]	mIM	1947	(Park <i>et al.</i> , 2006)
ZIF-11	[ZnN ₄]	bIM	1676	(Park <i>et al.</i> , 2006)
UiO-66	[Zr ₆ (μ ₃ -O) ₄ (μ ₃ -OH) ₄ (COO) ₁₂]	BDC	1187	(Cavka <i>et al.</i> , 2008)
UiO-67	[Zr ₆ (μ ₃ -O) ₄ (μ ₃ -OH) ₄ (COO) ₁₂]	BPDC	3000	(Cavka <i>et al.</i> , 2008)
UiO-68	[Zr ₆ (μ ₃ -O) ₄ (μ ₃ -OH) ₄ (COO) ₁₂]	TPDC	4170	(Cavka <i>et al.</i> , 2008)

Organic linkers are abbreviated as: BTC = benzene-1,3,5-tricarboxylate, BDC = terephthalate, BPDC = biphenyl-4,4'-dicarboxylate, BPTA = biphenyl-3,3',5,5'-tetracarboxylate, DHTA = 2,5-dihydroxyterephthalic acid, TPDC = [1,1':4',1''-terphenyl]-4,4''-Dicarboxylate, mIM = 2-methylimidazole and bIM= benzimidazole.

HKUST-1 is one of the most broadly investigated and well understood MOFs (Gascon *et al.*, 2008). HKUST-1 ($\text{Cu}_3(\text{BTC})_2$) is a copper-based MOF with benzene tricarboxylic acid ligands. HKUST-1 which is synthesised by the solvothermal method has a crystal size in the range of a few micrometres, usually 10 - 20 μm (Khan and Jung, 2009, Prestipino *et al.*, 2006). Nanoparticle crystal sizes of HKUST-1 can be obtained by ultrasonic or microwave methods for synthesis (Khan *et al.*, 2010, Khan and Jung, 2009). The BET surface area of HKUST-1 mostly ranges between 692-1500 $\text{m}^2 \cdot \text{g}^{-1}$ with a pore volume of approximately 0.34 $\text{cm}^3 \cdot \text{g}^{-1}$ (Li and Yang, 2008, Basu *et al.*, 2011, Chen *et al.*, 2013). The crystal structure of HKUST-1 MOF is graphically represented in Figure 2.11.

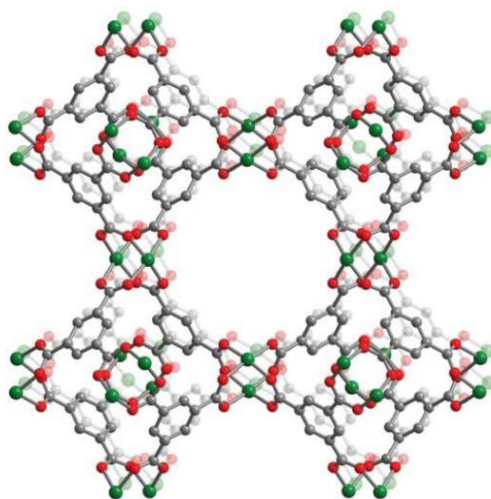


Figure 2.11: Crystal structure of HKUST-1 (Chui *et al.*, 1999).

Another interesting type of MOF include those with high flexibility to shape/change their structures. Flexible MOFs are able to reversibly change their frameworks when they interact with molecules (Wang *et al.*, 2016). One of the most common examples of flexible MOFs is MIL-53. MIL-53 exhibits a flexible framework with noted breathing effects during adsorption/desorption processes (Basu *et al.*, 2011). MIL-53 has the ability to open its pores when specific molecules such as CO_2 and H_2O are introduced (Wang *et al.*, 2016). MIL-53 demonstrates a narrow pore formation when adsorbing

molecules and opens to form large pores when desorbing molecules as graphically presented in Figure 5.3. MIL-53 is hydrophilic in nature and acts as a water stable MOF with 1D diamond-shaped pores and an internal diameter of 0.85nm (Basu *et al.*, 2011, Férey *et al.*, 2003, Llewellyn *et al.*, 2006). MIL-53 exhibits a high thermal stability of up to 500°C with a BET surface area and bulk density of $\approx 1000\text{m}^2 \cdot \text{g}^{-1}$ and $0.4\text{g} \cdot \text{cm}^{-3}$, respectively (Rallapalli *et al.*, 2011, Loiseau *et al.*, 2004, Finsy *et al.*, 2009). The crystal structure of the MIL-53 MOF is shown in Figure 2.12.

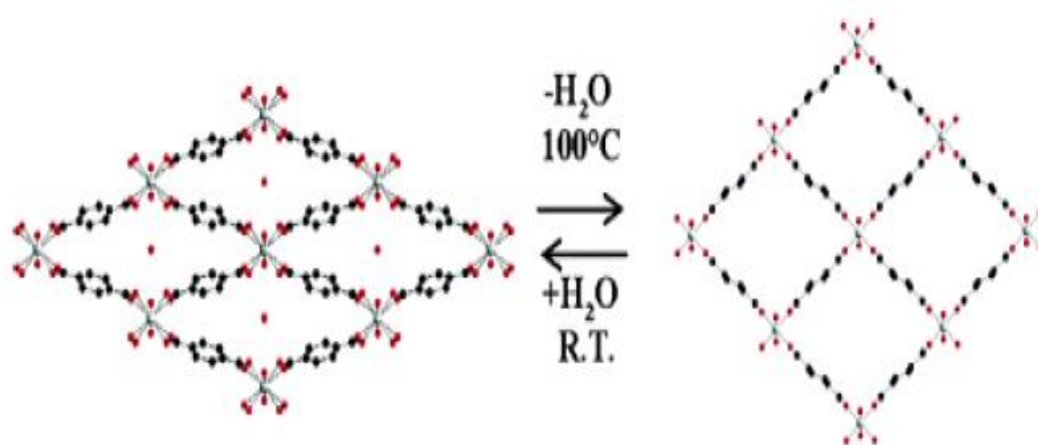


Figure 2.12: (Right) Dehydrated MIL-53, and (Left) Hydrated MIL-53 (Bourelly *et al.*, 2005).

MOFs have been used in MMMs through their incorporation into polymers to improve particle-polymer adhesion due to the presence of the organic linker in the structure of MOFs (Wang *et al.*, 2018). Furthermore, the addition of MOFs into polymers have the capability to improve separation performance. The functionalisation of MIL-53 into polysulfone to prepare nanocomposite membranes has been investigated by Zornoza *et al.* (2011). SEM images obtained in the study showed excellent adhesion between MIL-53 and polysulfone polymer, especially at a high MIL-53 loading of 40wt%. In addition, the selectivity of CO_2/CH_4 was also improved due to the flexibility of the structure of MIL-53. In a different study, Jeazet *et al.* (2012) incorporated several types of MOFs which includes HKUST-1, MIL-101, MIL-53, ZIF-8 and MOF-5 into polyimide and

polysulfone polymers to manufacture MMMs for gas separation applications. Results showed that MOFs have been successfully incorporated into the polymers. The permeability and selectivity increased for most cases compared to pure polyimide and polysulfone membranes. Incorporation of MOFs in polymers enables improvements in terms of the permselectivity of membrane's by prompting sorption and diffusion rates at a greater level of intensity (Car *et al.*, 2006). Basu *et al.* (2009) studied the effect of adding MOFs, specifically ZIF-8, HKUST-1 and MIL-53, into a Matrimid® polymeric matrix. Dense and porous membranes were prepared as a result of their study for CO₂ separation from N₂ and CH₄. Results demonstrated that both selectivity and permeability improved with MMMs compared to pure polymeric membranes. Additionally, membranes prepared with MIL-53 exhibited good interactions between CO₂ and MIL-53 due to the breathing behaviour of MIL-53. The fabrication of MMMs for gas separation by incorporating 0-40wt% loading of HKUST-1 into a polydimethylsiloxane matrix was studied by Car *et al.* (2006). Higher fluxes were observed for all gases with a higher selectivity being determined with 10wt% HKUST-1 loading compared to pure polymers.

The fabrication of MMM through the incorporation of MOFs into biopolymers was also considered. The manufacturing of dense MMMs with 5wt%, 10wt% and 20wt% HKUST-1 loaded PLLA/HKUST-1 was investigated by Kathuria (2013). The aforementioned study concluded that HKUST-1 was successfully incorporated into PLLA matrix with up to 20wt% HKUST-1 loading. The same author also reported that CO₂ permeability improved by 38% for 20wt% HKUST-1 loaded MMM compared to pure PLA films. Vinu *et al.* (2018) examined the incorporation of Al-MOF into chitosan biopolymers with 2.5wt%, 5wt% and 10wt% Al-MOF loadings to produce porous chitosan/Al-MOF MMMs for water/ethanol mixture separations. Results from their

study showed that separation performances improved for most membranes, with the highest flux and separation factor exhibited by the chitosan/Al-MOF MMM loaded at 5wt% Al-MOF. The flux and separation factor increased from $383\text{ g m}^{-2}\text{ hr}^{-1}$ to $623\text{ g m}^{-2}\text{ hr}^{-1}$ and 240 to 1369 respectively in comparison to pure chitosan membranes. The incorporation of 3D aluminium MOF into chitosan biopolymer membranes for ethanol/water separation was successfully attained in a previous study (Vinu *et al.*, 2019). Results indicated that the flux and separation factor increased for some selected membranes. The fabrication of MMMs via the incorporation of MOFs into biopolymers is a very attractive scope of membrane research due to the biodegradability and sustainability of biopolymers in addition to the potential improvements in terms of the MOFs particle-polymer adhesion in MMMs.

2.8 Biopolymers

Biopolymers or ‘natural polymers’ are derived directly from the animals or plants (Rendón-Villalobos *et al.*, 2016). Biopolymers have shown great potential to be used in various applications such as food processing and separation processes (Telis, 2012). The medical field and packaging are also some of the application areas for biopolymers (Sampath *et al.*, 2016). One of the most important properties that distinguish natural polymers from other types of materials and petroleum-based polymers is their sustainability. Biopolymers are biodegradable, biocompatible and non-toxic (Vroman and Tighzert, 2009). In addition, additives can be incorporated into biopolymers to enhance and control their mechanical strength and stability (Bakar and Tan, 2016). Several types of natural polymers have been investigated for use in separation-related applications. The most common, applicable and promising types of natural polymers are chitosan, polylactic acid and cellulose (Mansoori *et al.*, 2020, Thakur and Voicu, 2016).

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Cellulose is a biopolymer that is mainly derived from wood and cotton (Kabsch-Korbutowicz, 1999, Kim et al., 2016). In the 1960s, cellulose and its derivatives have been explored for use in the field of water purification membranes (Lee *et al.*, 2016). The first commercial cellulose-based membranes were fabricated for RO applications (Yang *et al.*, 2019b). Improvements in thermal stability, mechanical strength and separation performance of a membrane can be attained by adding selected types of additives (Shaari and Kamarudin, 2019). Sodium dodecyl sulfate (SDS) was added to modified coal and other additives to be incorporated into cellulose membranes to modify the hydrophilicity and surface porosity thus improving the permeability (Ahmad et al., 2016a). Bai (2012) demonstrated that the addition of TiO_2/ZnO into cellulose membranes enhanced antifouling properties and increased the flux.

Chitosan is another common type of biopolymer that has been widely used in various applications i.e. as a membrane, stabiliser and as an adsorbent (Toledo, 2015). Chitosan is a result of the deacetylation of the biopolymer chitin (Elieh-Ali-Komi and Hamblin, 2016). Chitosan can be shaped easily in different forms thus allowing the control of the surface area and porosity (Bakar and Tan, 2016). Additives can be incorporated into chitosan membranes to enhance separation performance as well as their respective mechanical properties (Salehi, 2013, Sawalha et al., 2007). Zinadini (2014) studied the effects of adding carboxymethyl chitosan/ Fe_3O_4 nanoparticles into PES NF membrane via the phase inversion method. Higher water flux and permeation in addition to good antifouling properties were observed in comparison to unmodified PES membranes.

Another common biopolymer that has been widely used in several applications is PLA. PLA is derived from bio-sources such as corn and sugar (Moriya *et al.*, 2009). PLA is a thermoplastic polymer and therefore has a high potential to replace some of the traditional polymers such as PC, PS and PET (Jamshidian *et al.*, 2010). PLA has been

used in a variety of medical applications that include tissue engineering scaffolds, drug delivery and haemodialysis (Domingues *et al.*, 2016). Moreover, PLA has also been used in packaging, the food industry, textile applications and film manufacturing (Garlotta, 2001, Yu *et al.*, 2015, Gupta *et al.*, 2007). Jamian *et al.* (2015) prepared PLA films for gas separation using the phase inversion method. In their study, the films were successfully fabricated and gas permeation tests were successfully performed. However, the aforementioned films were not ready for commercialisation as further investigations and improvements needed to be done. Many studies have extended the capabilities in processing PLA by reinforcing it using nanofillers such as MOFs, metal oxide nanoparticles, clays, chitin nanofibers or cellulose nanocrystals (Díez-Pascual, 2019, Dai *et al.*, 2017).

Comparing between cellulose, chitosan and PLA, cellulose has limited applications as it is environmentally unsustainable and has a high cost of modification (Yang *et al.*, 2019a). In addition, low yields of bacterial cellulose is also a key drawback of the cellulose biopolymer (Chawla *et al.*, 2009). Chitosan on the other hand is a promising biopolymer for various applications with a few already available commercial industrial plants for chitosan production (Kumar, 2000). However, chitosan production is considered to be an aggressive process due to complexities in chemically extracting chitin (Roberts, 1997). Homayoni *et al.* (2009) also reported the problematic nature in the production of chitosan due to it being insoluble in organic solvents, forms strong hydrogen bonds and is characterised as ionic in solutions. Enzyme hydrolysis or a fermentation process can be used to produce chitin despite these processes being very costly at an industrial scale (Win and Stevens, 2001). However with the production of PLA being well-understood and developed, PLA has been commercially produced by various companies (Doug, 2010, Ravenstijn, 2010). One of the key drivers in the usage

of PLA is that the polymer is considered to be one of the best alternatives to petroleum-based polymers such as PS due to its thermoplastic behaviour (Mishra, 2018, Mokhena *et al.*, 2018). Hence, PLA has a high potential to be used in several industries such as packaging, cosmetic, medicine and engineering sectors (Díez-Pascual, 2019, Hajba *et al.*, 2015).

PLA biopolymer

PLA is a bio-based polymer belonging to the aliphatic polyesters family and is derived from natural sources such as corn, starch and sugar (Elangovan *et al.*, 2011). Similar to conventional thermoplastic polymers, PLA has been commercially processed using blown film moulding, film forming sheet extrusion, injection moulding, cast film and thermoforming (Modi, 2010, Doi and Steinbüchel, 2002). The physical, mechanical and chemical properties, crystallinity, the crystal structure and mass transport properties of PLA is influenced by its isomeric composition (Södergård and Stolt, 2002, Cocca *et al.*, 2011, Tsuji, 2005).

The constituent unit of PLA is lactic acid (2-hydroxypropionic acid). The two main common types of PLA isomers are poly(L-lactic) (PLLA) and poly(D-lactic) (PDLA) for which PLA consisting of both D and L isomers are referred to as poly(D,L-lactic acid) (PDLLA) (Sawalha *et al.*, 2007, Garlotta, 2001). The chemical structures of L-lactide acid and D-lactide acid isomers are shown in Figure 2.13.

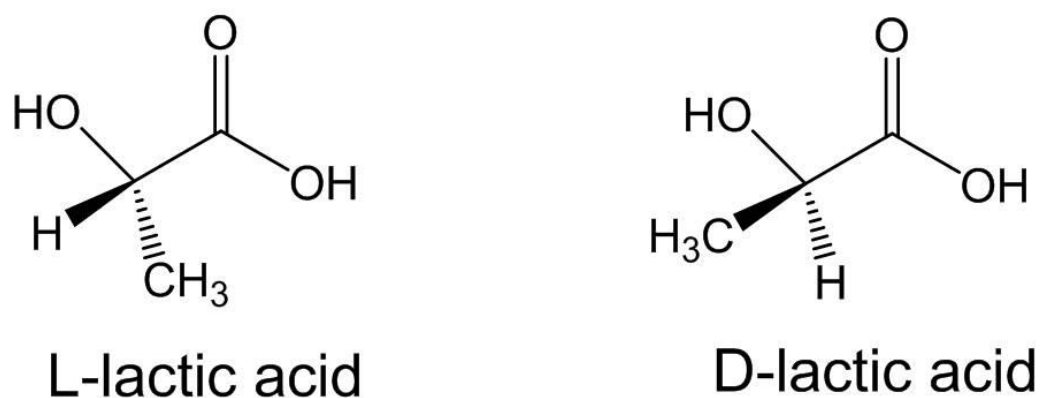


Figure 2.13: L-lactide acid and D-lactide acid isomers.

With PLLA exhibiting a crystalline structure and PDLLA exhibiting an amorphous structure, the aforementioned isomers are either in a glassy or rubbery state (Sawalha *et al.*, 2007). PLA is considered to be semi-crystalline when it contains more than 93% L-lactic acid but is considered to be amorphous when the L-lactic acid content is between 50-93% (Auras *et al.*, 2004). PLLA has a higher thermal stability and better mechanical properties compared to PDLLA due to its crystalline structure (Van de Witte *et al.*, 1996). PLA can be fully amorphous and crystallised using a melt-quenched heating technique (Jia *et al.*, 2009). The influence of variations in L/D isomer ratio of PLA in relation to the glass transition (T_g) and melting (T_m) temperatures is represented in Table 2.5. As the L/D isomer ratio increased, the T_g and T_m temperatures increases thus implying that the thermal properties is higher as the crystallinity of PLA increases. The monomer lactic acid can be obtained from renewable resources such as corn and sugar via microbial i.e. bacterial fermentation processes (Juturu and Wu, 2016, Msuya *et al.*, 2017). Depending on the microbial strain used during the fermentation process, a D-lactic acid or L-lactic acid can be attained (Babu *et al.*, 2013).

Table 2.5 Variation in T_g and T_m of PLA corresponding to various L/D isomer ratio. (Garlotta, 2001).

PLA L/D ratio	T_g (°C)	T_m (°C)
100:0	63	178
95:5	59	164
90:10	56	150
85:15	56	140
80:20	56	125

The most common technique used to synthesise PLA is via the ring-opening polymerisation of lactide monomer or by direct polycondensation reaction of lactic acid (Babu *et al.*, 2013). The technique of implementing polycondensation reaction does not obtain PLA exhibiting a high molecular weight due to the formation of water during synthesis (Babu *et al.*, 2013). To produce a continuous process of obtaining high molecular weight PLA at low cost, a two-step synthesis process is required (Vink *et al.*, 2007). In the first step, a polycondensation reaction process is used to synthesise PLA exhibiting low molecular weight. In the subsequent step, the ring-opening polymerisation process with selected catalysts is then used to convert the pre-PLA polymers into high molecular weight PLA. A commercial continuous process for PLA production developed by NatureWorks Company is illustrated in Figure 2.14.

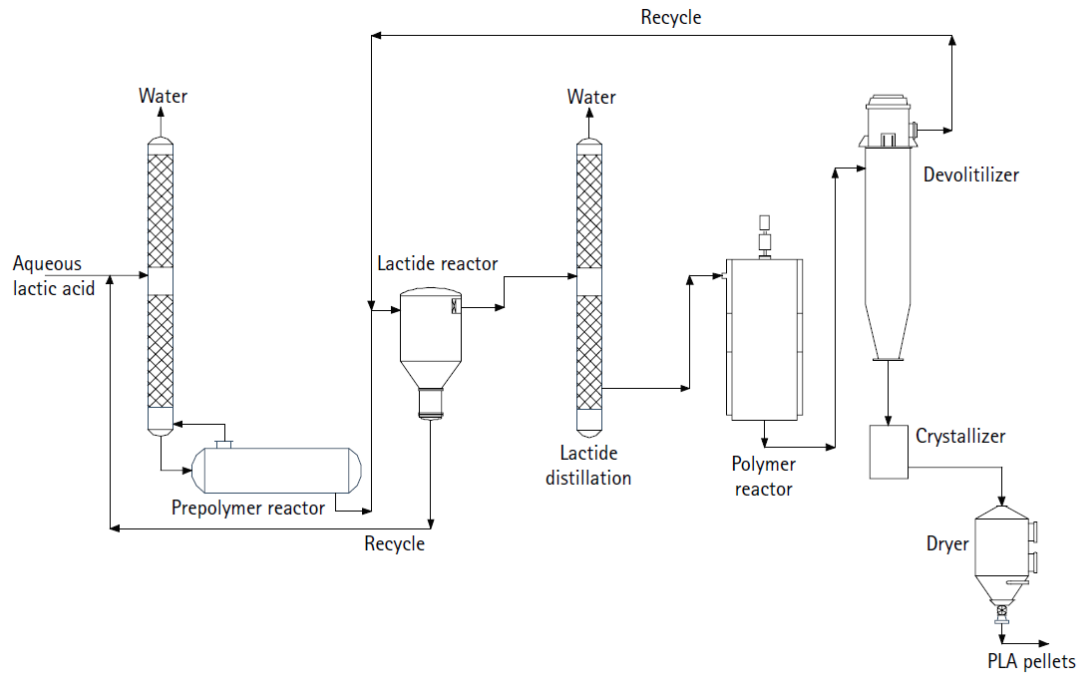


Figure 2.14: Lactide formation and polylactide polymerisation continuous process developed by NatureWorks (Vink *et al.*, 2007).

The degradation time of PLA biopolymers has been studied using various grades of PLA, solution medium and testing/analysis methods. In general, the degradation rate increases with increasing polymeric porosity and exposed surface area. Increase in crystallinity, molecular weight and mass would lead to a decrease in the rate of degradation (Middleton and Tipton, 2000, Törmälä *et al.*, 1997, Gogolewki, 1992, Voutilainen *et al.*, 2002). Regardless of environmental conditions such as temperature and solution medium, the range of required degradation time for some common biopolymers are presented in Table 2.6. Compared to other biopolymers, PLA has a relatively long degradation time for complete resorption due to its slow degradation rate (Gajjar and King, 2014). Amorphous PLA degrades in 12-36 months while crystalline PLA takes 24-72 months for complete resorption (Middleton and Tipton, 2000, Gogolewski, 2000).

Table 2.6: Comparison of degradation times for complete resorption of some common biopolymers. PCL: poly(ϵ -caprolactone), PGA: poly(glycolide), PLA: poly(L-lactic acid). (Middleton and Tipton, 2000, Woodruff and Hutmacher, 2010, Gogolewski, 2000).

Biopolymers	PCL	PGA	PLA
Degradation time (month)	24-48	6-12	1-72

The degradation of polymers occurs mainly by four routes; thermal, mechanical, hydrolytic and radiation (Kulkarni and Dasari, 2018, Scaffaro *et al.*, 2019). Mechanical degradation occurs as a result of applied stress or compression on the polymer during use i.e. screws (Farah *et al.*, 2016, Shojaeiarani *et al.*, 2019). The manufacturing/processing of polymers at a high temperature especially above the melting temperature for a long period of time leads to thermal degradation (Heredia-Rivera *et al.*, 2019, Shojaeiarani *et al.*, 2019). Gamma radiation is one of the most common techniques used to sterilise polymers which causes radiation degradation (Harrell *et al.*, 2018). Hydrolytic degradation refers to water hydrolysis or enzymatic hydrolysis in the biological environment whereby weak bonds of a polymer chain reacts with water molecules to break up resulting in smaller polymer chains (Lyu and Untereker, 2009, Felfel, 2013). Biodegradable polymers mainly degrade hydrolytically in two stages (Göpferich, 1996, Felfel, 2013). The first stage takes place directly after the attachment of the polymeric specimen to water wherein water molecules cut the long chains into many short chain oligomers. As a result, the molecular weight of the polymer decreases and as a consequence results in the loss of mechanical strength. The second stage can be observed through the mass loss of the polymer. A sequence of hydrolytic degradation profiles are presented in Figure 2.15.

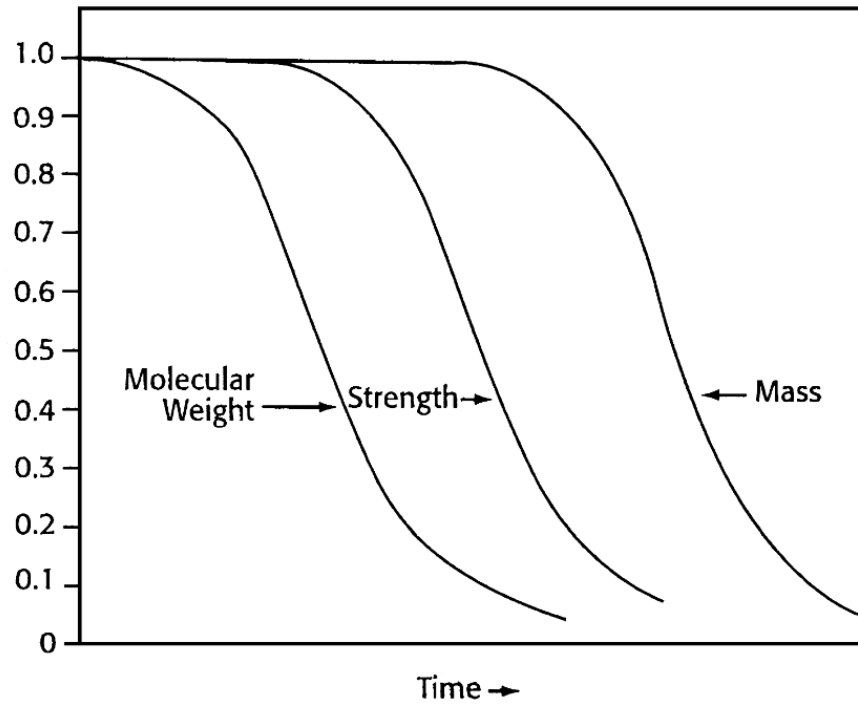


Figure 2.15: Sequence of reduction in molecular weight, mechanical strength and mass of biopolymers over time during degradation (Middleton and Tipton, 2000).

In comparison to all other biopolymers, PLA has one of the highest mechanical strengths and heat resistance (Babu *et al.*, 2013). The mechanical performance of PLA is comparable to petroleum-based polymers since PLA has high stiffness and is capable of being shaped (Smith, 2005). In addition, it also exhibits thermoplastic behaviour with a high elastic modulus (Garlotta, 2001, Domingues *et al.*, 2016). The mechanical properties are dependent on several factors such as film porosity, crystallinity, thickness and processing/fabricating technique (Liao *et al.*, 2019, Bernards and Desai, 2010, Council, 1994). In a study by Pande *et al.* (2020), low porosity PLA films fabricated using an evaporation technique exhibited a tensile stress and Young's modulus of approximately ~25 and ~17MPa respectively. Hollow fiber PLA films characterised with high porosity exhibited a tensile stress of 3.49MPa (Moriya *et al.*, 2009). Higher L-lactide units result in higher tensile strength and elongation at break value (Modi, 2010). The excellent thermal processing capability of PLA in comparison to other biopolymers makes it suitable for various polymer processing techniques such as film

extrusion, film forming, fibre spinning, thermoforming, injection moulding and blow moulding (Auras *et al.*, 2004). Its biocompatibility in particular makes it a suitable fit for medical applications e.g. use in the human body and human-related applications since it does not produce any toxic substances during use (Rasal *et al.*, 2010). Over a 50% reduction in energy consumption can be reached when petroleum-based polymers are replaced by implementing PLA biopolymers thus making them a highly desirable field for research (Farah *et al.*, 2016, Rasal *et al.*, 2010). It has already been proven that PLA has the potential to replace conventional petroleum-based polymers for industrial applications such as food packaging, film fabrication and medical applications due to the previously mentioned attributes in addition to its comparatively lower cost, non-toxicity and ease of processing in nature (Khuenkeao *et al.*, 2016, Lopes *et al.*, 2012, Fehri *et al.*, 2016, Akindoyo *et al.*, 2017).

Despite the above, PLA has some drawbacks that limit its use in certain applications. Key limitations associated with PLA are low heat deflection temperature, low gas barrier properties and poor tear resistance (Ahmed and Varshney, 2011, Dorgan *et al.*, 2000, Rasal *et al.*, 2010). In addition, PLA suffers from relatively low thermal stability compared to other polymers, typically 300-400°C, due to its low degree of crystallisation (Khuenkeao *et al.*, 2016, Fehri *et al.*, 2016). Another issue with PLA is that it has no reactive side-chain group which limits its capabilities for surface modifications (Farah *et al.*, 2016). The slow degradation rate of PLA in an atmospheric environment is also considered to be one of its main disadvantages as it has a relatively long lifespan which may reach several years, typically 3-5 years under certain conditions (Rasal *et al.*, 2010). The degradation rate of PLA depends on many factors including PLA crystallinity, D-lactide/L-lactide isomer ratios, molecular weight, the diffusion rate of water in PLA and morphology (Janorkar *et al.*, 2004). PLA has poor toughness and

is brittle that is it does not elongate beyond its breaking point to more than 10% of its original length (Rasal and Hirt, 2009). Characteristics and properties of PLA i.e. toughness and stiffness can be improved using various methodologies such as filler additives, plasticisation, copolymerisation, reactive extrusion and melt blending (Liu and Zhang, 2011, Martin and Avérous, 2001, Grijpma and Pennings, 1994, Ray and Okamoto, 2003, Bhardwaj and Mohanty, 2007). Fabrication of MMMs with PLA was addressed using HKUST-1 MOF particles by Kathuria (2013) in a study that reported enhancements in toughness and stiffness of the final matrix from the addition of HKUST-1 particles into a dense matrix of PLA biopolymer.

2.9 Past and current state of water purification membranes

Conventional membrane materials (inorganic and organic membranes) have been widely used in the sector for water purification membranes. Organic/polymeric membranes have been applied in a wide range of applications including water treatment and desalination (Kayvani Fard *et al.*, 2018, Ulbricht, 2006). In many water treatment processes, porous polymeric membranes are used for MF and UF applications (Zhu *et al.*, 2018). Porous polymeric membranes have also been used as a pre-treatment for NF and/or RO membranes to reduce fouling (Basile *et al.*, 2019, Bazargan, 2018). In general, most of these membranes have an asymmetric structure with a less porous layer on top of a porous support layer (Han and Steckl, 2009). There are some common polymeric membranes that have been used in water treatment and desalination applications which have shown high selectivity, permeability and stability in water (Pendergast and Hoek, 2011). These include PP, PAN, PTFE, PVDF, PES, PDf, CA, PA and sulfonated PES or PSf (Zahid *et al.*, 2018, Pendergast and Hoek, 2011).

In the 1980s, knowledge in regards to inorganic membranes (i.e., ceramic) has grown and MF and UF membranes were applied in industrial separations (Bhave, 1991).

Chapter 2: Literature Review

Ceramic, carbon, silica and zeolite are some of the common inorganic materials that have been explored in water membrane applications (Kayvani Fard *et al.*, 2018). Sol–gel processing is the most popular and useful technique used to fabricate inorganic membranes (Agoudjil *et al.*, 2008, Uche, 2013). In addition, some coating techniques have been applied to enhance the performance, mechanical strength and stability of membranes (Hassan, 1995). Inorganic membranes such as ceramic are suitable for challenging water purification processes due to its advantages such as long membrane lifetime and ease of cleaning after fouling (Benito, 2007). However, the cost is very expensive especially at a large scale which limits their applications (Faibish, 2001).

Thin film composite (TFC) membranes is one of the most traditional and common type of composite membranes that has been mostly applied in NF and RO membrane applications (Ismail *et al.*, 2015). TFCs are formed with an ultra-thin dense layer polymerised on top of a porous polymeric support membrane (Feijani *et al.*, 2015). Independent selection of the dense ultra-thin layer and the porous support layer in terms of their performance is considered a key advantage of implementing TFC over integrally skinned asymmetric membranes to obtain optimised composite membrane performance (Rao, 1997). Over the past 50 years, TFC membranes have been developed and widely used as RO membranes due to the high flux and high selectivity for seawater desalination, and their low pressure for desalting brackish water (Pendergast and Hoek, 2011). TFCs were also developed to be used in NF membranes for the removal of dissolved organic particles and to soften water (Basile and Comite, 2020).

One area of recent ongoing research in the field of membranes is the fabrication of nanotechnology-based membrane materials. The most common and developed nanotechnology-based materials are nanostructured ceramic and inorganic-organic membranes (Pendergast and Hoek, 2011). Thin film nanocomposite (TFN) membranes

have been broadly used in which nanoparticles are added to TFC membranes to enhance membrane performance (Wang *et al.*, 2017). As with the case with TFCs, TFN is largely used for NF and RO membranes (Adamczak *et al.*, 2019). However, TFN membranes have antimicrobial activity, lower fouling and better separation performance in comparison to TFCs (Lind, 2009, Jeong, 2007).

MMMs are a very promising class of composite membranes that has been gaining high attraction in the research field of both gas and liquid membrane separation applications (Lewis, 2019). A considerable number of research studies have investigated the gas separation potential of MMMs with only a few studies having concentrated on liquid separation and water purification applications (Verma *et al.*, 2019). The new trend in membrane research is to implement MMMs into water membranes (Goh *et al.*, 2016, Figoli *et al.*, 2017).

The addition of nanofibers as MMMs has a high influence on membrane performance and properties. Fan (2008) used a commercial UF membrane, PS, and showed that the addition of polyaniline (PANI) nanofiber particles resulted in higher selectivity and permeability for bovine serum albumin (BSA). In addition, improvements in terms of flux recovery and antifouling properties were also found. Another study showed that the addition of alumina nanoparticles into PVDF membranes increased the hydrophilicity, water permeability and mechanical strength of MMMs for UF applications by separating proteins of different molecular weight (Yan, 2005). In addition, they observed an increase in flux recovery and reduction in fouling rate. Pendergast (2010) demonstrated that incorporating zeolite and silica to PSf RO membranes for salty water separation i.e. separating NaCl, exhibited higher water permeation, better open surface pores in addition to less flux decline in comparison to pure PSf supported membranes.

The implementation of MMMs using biopolymers has also been recently considered. Xu (2013) reported that the addition of laccase enzyme to chitosan/poly(vinylalcohol) nanofibrous membranes improved the mechanical properties of chitosan membranes. Saranya *et al.* (2014) studied the influence of incorporation iron oxide and activated carbon into CA membrane with loadings of 0.5, 1.5 and 2.5 wt%. Results showed significant improvement in the water flux and membrane crystallinity in all cases of CA/activated carbon MMMs. However, incorporation of iron oxide particles into the CA membrane, CA/ iron oxide MMMs, has reduced water flux and crystallinity at loadings of 1.5 and 2.5%. Dai *et al.* (2016) incorporated ZIF-8 MOF nanoparticles into PLA to fabricate electrospun nanofiber membranes for oil/water separation. Results showed that PLA/ZIF-8 membranes presented a high separation efficiency for octane/water mixtures, hexane/water and diesel/water mixtures and thus are potential candidates for oil/water separation. In addition, they found that the mechanical properties have also significantly improved for PLA/ZIF-8 membranes compared to pure PLA membranes. Up to date, only a few studies have investigated the fabrication of MMMs with biopolymers especially for liquid separation and water purification applications. With the above, it shall be noted that the manufacturing of biopolymer-based MMMs for liquid membrane applications such as water purification is still in its infancy and hence has a high potential to be explored in the future.

2.10 Research scopes

Many researchers have investigated various types of membranes, materials and fabrication techniques for water treatment and remediation. However, most of these studies failed to fabricate cheap membranes with excellent separation performance and high mechanical strength. Several composite membranes formed from inorganic-polymeric materials have been studied to enhance the properties and performance of

membranes while further investigations are needed to understand the adherence between inorganic and organic materials as this consequently controls the microstructure of the membrane. Most of the commercial polymeric membranes purposed for water purification applications are made from petroleum-derived materials. Limited types of biopolymer materials have been explored for membrane applications.

In this project, the feasibility of using PLA biopolymer as the polymer phase in membranes purposed for water purification applications will be explored. Flat sheet porous membranes will be fabricated and studied at various preparatory conditions using the phase inversion via immersion precipitation technique. In addition, in order to enhance the mechanical and separation properties of membranes, the incorporation of MOFs into the PLA phase to form MMMs will be investigated. The relationship between organic-inorganic material chemistry, membrane microstructure, chemical/thermal stability, physical properties and mechanical properties in addition to separation performance will be examined for the novel fabricated membranes via material characterisation techniques.

Chapter 3: Methodologies

3.1 Materials

PLA2003D semi-crystalline biopolymer ($M_w \approx 200\text{kDa}$) was supplied by Ingeo™ Biopolymer. PLA2003D polymer contains 4 - 4.5% D-Lactide (Gwon *et al.*, 2016). RESOMER LR708 S amorphous PLA biopolymer ($M_w \approx 1500\text{kDa}$) was supplied by Evonik. Dimethyl sulfoxide (DMSO) with a purity of $\geq 99.5\%$ was supplied by Sigma-Aldrich and used as a solvent. Methanol with a purity of 99.99% was supplied by Fisher Chemical. Methanol and distilled water were used as non-solvents. HKUST-1 and MIL-53 metal-organic frameworks (MOFs) were used as inorganic materials. HKUST-1 and MIL-53 MOFs were supplied by the University of Nottingham, Advanced Materials Research Group. Direct supplier of HKUST-1 and MIL-53 MOFs is Sigma-Aldrich. The particle size of HKUST-1 and MIL-53 ranged between 1 – 10 μm and 0.5 – 5 μm , respectively as shown in Figure 3.1.

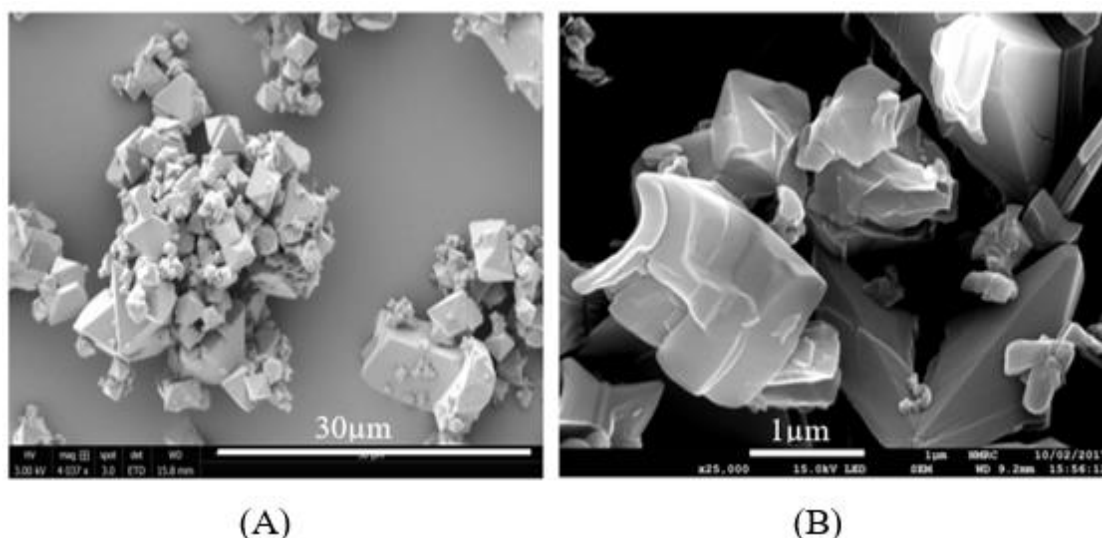


Figure 3.1: SEM images of (A) HKUST-1 and (A) MIL-53 MOFs.

3.2 Pre-treatments of PLA pellets

Before preparing the PLA films, raw “PLA pellets” were pre-treated and classified into three different groups; (1) as received ‘pure’ pellets, (2) dried pellets and (3) quenched pellets. Pure pellets were used to immediately prepare the PLA film without any prior process/treatment to the pellets. Dried pellets were dried overnight at 100 °C to remove any moisture. Melted pellets were heated to 220 °C for 45 minutes, then quenched immediately in a cold water bath at ≈ 5 °C, in order to reduce initial crystallinity.

3.3 Film fabrication

There are various techniques for film fabrication. Based on the film application, the appropriate fabrication technique can be selected. This study seeks to produce a usable asymmetric membrane that is porous and semi-permeable for applications in water filtration.

The most common commercial and understood film fabrication method that produces an asymmetric porous membrane is the phase inversion by immersion precipitation technique. In this technique, the mixture is cast onto a non-woven substrate, and then submerged in a non-solvent based coagulation bath. Consequently, precipitation takes place due to phase exchange between the solvent and non-solvent as graphically represented in Figure 3.2. The polymer have to be soluble in the solvent. The morphological structure of the resulting membrane depends on several factors such as the type of polymer, the type of solvent and nonsolvent used, the polymer concentration, the coagulation bath temperature and immersion time (Mulder, 1991).

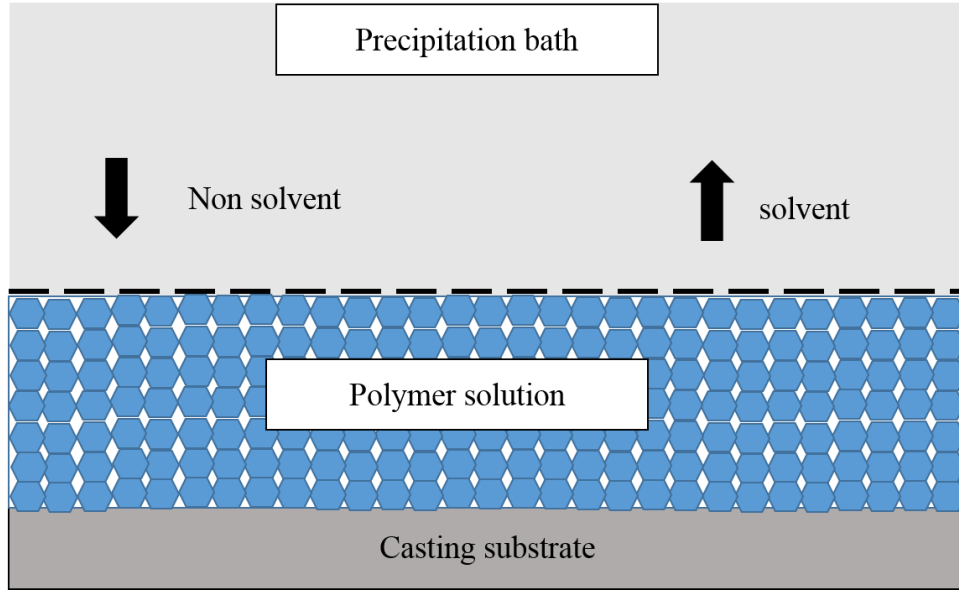


Figure 3.2: Phase inversion mechanism by immersion precipitation. Adapted from (Mulder, 1991).

In this study, the type of polymer used is fixed to be a PLA biopolymer. According to previous literature, DMSO is considered to be one of the most effective solvents used in dissolving PLA and is therefore selected to be the solvent (Legrand *et al.*, 2007, Maharana *et al.*, 2010). Water, methanol (MeOH) and 50/50 v/v% mixture of water/methanol were explored as non-solvent coagulation baths. This type of non-solvent showed a strong effect on the structural formation and characteristic properties of the films.

Hansen's graph is useful to predict whether a given liquid will be considered a solvent or a non-solvent for a polymer. If the solution is located inside a circle of less than five δ -units, then it is considered to be a solvent for polymers. However, if the solution is located outside the circle then that solution can be used as a non-solvent (Legrand *et al.*, 2007). Where; dispersion force component (δ_d), polar force component (δ_p), hydrogen bonding component (δ_h), combined the effects of δ_d and δ_p into one single parameter (δ_v) in equation 3.1 (Legrand *et al.*, 2007, Maharana *et al.*, 2010).

$$\delta_v = \sqrt{\delta_d^2 + \delta_p^2} \quad (3.1)$$

As seen in Figure 3.3, the PLA polymer is expected to be soluble in DMSO and insoluble in water and methanol. Considering Figure 3.2, the solvent diffuses in a non-solvent bath and vice versa, and as a result of this precipitation taking place, the polymer solidifies to form a film. The solubility of PLA in methanol is relatively higher than in water. Therefore, the conclusion can be made that DMSO-water, DMSO-methanol and DMSO-water/methanol systems may affect the kinetics for solvent-exchange and thus the structure of the films formed.

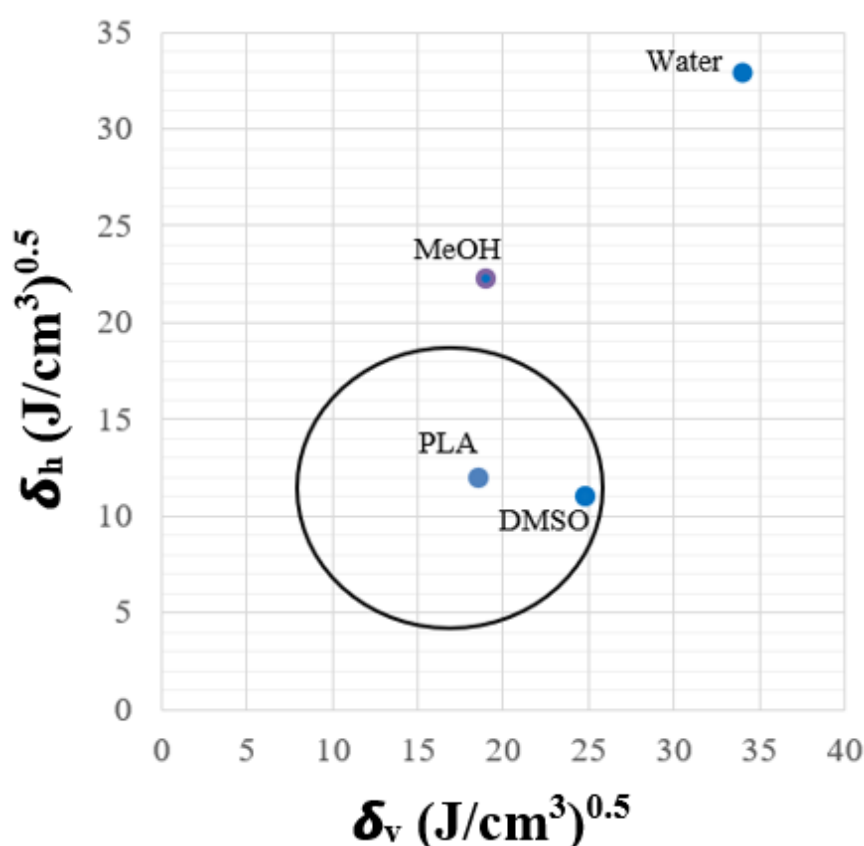


Figure 3.3: Hansen's two-dimensional graph of partial solubility parameters of solvents with respect to the partial solubility parameter determined for PLA.

For a typical procedure in the preparation of PLA films, 0.5-2.0g of either pure, dried or melted PLA pellets and 8.0-9.5g of solvent were weighed in a glass vial. The solution was mixed with a magnetic stirrer at 80°C for 24 hrs. The polymer/solvent ratio was changed between 5/95 – 20/80wt/wt%.

For the PLA/MOFs MMMs, films were prepared by incorporating 5 – 40wt% MOF in PLA. In terms of typical preparation of PLA/MOFs films, 0.05-0.40g of MOF and 9g of solvent were weighed in a glass vial. The mixture was subsequently mixed with a magnetic stirrer at 80°C for 24 hours. Then, 0.60-0.95g of pure PLA pellets were dissolved in the resulting mixture at the same temperature for another 24 hours. The (Polymer+MOF)/solvent ratio was fixed at 10/90 wt/wt%.

For example, to prepare a film with 5% MOF in PLA with a total weight of materials equivalent to 10g, it requires:

Table 3.1: An example of preparation a film with 5% MOF in PLA matrix with a total weight of materials equivalent to 10g.

Materials	DMSO	PLA	MOF	Total
Amount (g)	9	0.95	0.05	10

After mixing, the homogenous mixture was cast onto a glass substrate via a micrometre headed blade. The casting thickness of the films were between 12.5-150µm. The casting method allowed the fabrication of a flat sheet membrane. The substrate with the cast film was immediately immersed into the non-solvent coagulation bath for 10 minutes to 24 hours at room temperature for phase inversion. The non-solvent bath contained water and either methanol or water/methanol 50/50 v/v%. Subsequently, the resulting membrane was removed from the substrate and placed in a drying oven for 24 hours at 40°C. After the drying step, the film was deemed ready for further tests.

It important to note that two methods for drying were explored. The first method is to place the film in a normal/conventional drying oven for 24 hours at 40 °C. The second method is to subsequently place the film in a vacuum oven for 24 hours at 25 °C after

drying the film for 24 hours at 40 °C in a normal drying oven. The reason behind the addition of the vacuum oven in the process of drying is to investigate if the solvent, methanol and any present moisture is fully removed via the normal drying oven or if the vacuum oven step is essential in fully removing the solvent, methanol and moisture. In regards to the above, the drying temperature was selected to be 40 °C in consideration of the freezing point of the solvent, DMSO, being ≈ 19 °C; and the glass transition temperature of the PLA polymer being ≈ 60 °C (Khuenkeao *et al.*, 2016). The selected temperature must be higher than the solvent freezing temperature to ensure no solvent is frozen and trapped within the pores of the film. The temperature must also be lower than the glass transition temperature of PLA as it is critical to not have any changes to the polymer's morphological characteristics during drying.

A 5% PLA concentration value was selected to study two aspects that may have some influence on the characteristics of the film. Firstly, pure polymer pellets were dried at 100°C overnight and subsequently used to prepare films under the same conditions using a matching technique. The aim of this experiment is to verify whether moisture plays a role in the fabrication conditions and final properties of the film. In the second experiment, a few grams of pure polymer pellets were placed in aluminium foil and melted at 220°C for 45 minutes in an oven before being immediately quenched in a cold water bath at ≈ 5 °C for 20 minutes. Resulting melted PLA pellets were used to prepare the films under the same conditions using a matching technique. This melting-quenching technique was considered to reduce the initial crystallinity. With this, the influence of the technique on the resulting properties of the films can be observed.

3.4 Characterisation

3.4.1 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) is a technique used to examine the microstructure and morphology of the surfaces of membranes as well as their cross section. This gives the opportunity to evaluate pore channel size and distribution. Additionally, the thickness of the membrane can also be estimated. Membrane samples were placed in a liquid nitrogen bath for a few seconds before being fractured. The samples were coated using a sputter coater to obtain a ~15nm thick layer of gold for 240 seconds prior to SEM analysis. The SEM instrument model is JEOL JSM-6060LV (JEOL Ltd., Japan).

3.4.2 Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) analysis was performed using Discovery DSC 2500 (TA Instruments, Delaware, USA). Samples of a few milligrams, ≈ 5 -10mg, were placed into sealed aluminium pans. The samples were brought down to a temperature of 0°C. Subsequently, samples were heated up to 220°C then cooled back down to 0°C at a heating/cooling rate of 10°C/min. Each sample was examined in two cycles as shown in Figure 3.4. The glass transition temperature (T_g), crystallisation temperature (T_c), melting temperature (T_m) and degree of crystallinity (χ_{DSC}) were calculated from both the first and second heating cycles. An example of a heat flow thermogram for PLA and the determination of its respective thermal properties are shown in Figure 3.5.

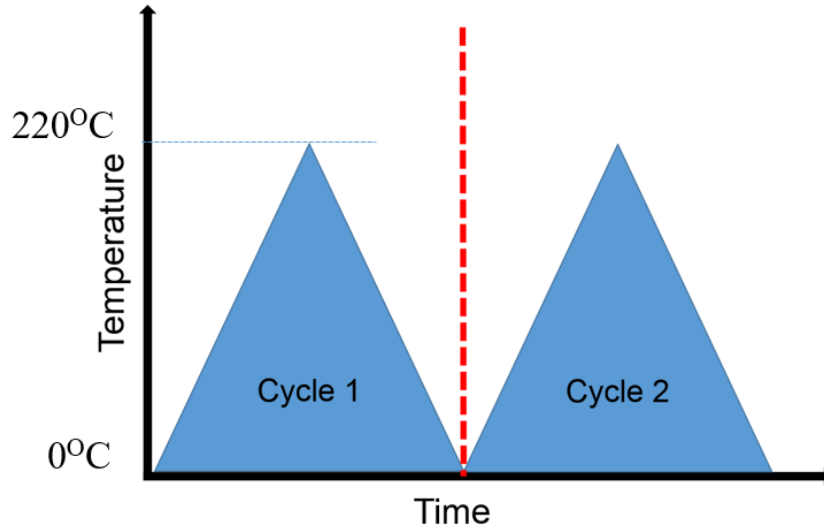


Figure 3.4: Schematic of the DSC heating cycles.

In DSC analysis, the first cycle expresses the thermal properties of the structure and manufacturing process. The original thermal properties of the material itself can be detected from the second heating cycle. Therefore in our analysis of PLA pellets, the data obtained from the second heating cycle was used to eliminate any thermal history that may have been caused due to storage or processing. On the other hand, the effect of fabrication conditions on the thermal properties of films was explored based on the first heating cycle. Crystallinity is the ratio of the measured heat fusion of a tested sample to the specific heat of fusion corresponding to 100% crystallinity of PLA. Thus, crystallinity can be calculated as follows:

$$\chi_{\text{DSC}} = \frac{\Delta H}{\Delta H_f} \quad (3.2)$$

For $\Delta H(\text{J/g}) = \Delta H_m - \Delta H_c$, where H_m and H_c are the heat enthalpy of melting and crystallisation respectively. H_m and H_c were determined from the area under the melting and crystallisation peaks within a fixed temperature range between 75°C to 180°C using the DSC 2500 software tool. ΔH_f is the heat fusion at 100% crystallinity which was determined to be 93J/g for PLA based on previous literature (Akindoyo *et al.*, 2017, Fehri *et al.*, 2016).

For the PLA/MOFs MMMs, the percentage of MOF incorporated into the PLA matrix was taken into account in the calculations for crystallinity. ‘X’ refers to the incorporated MOF weight fraction in a PLA matrix. The crystallinity of PLA/MOFs MMMs can be calculated using the following equation:

$$\chi_{DSC} = \frac{\Delta H}{\Delta H_f (1-X)} \quad (3.3)$$

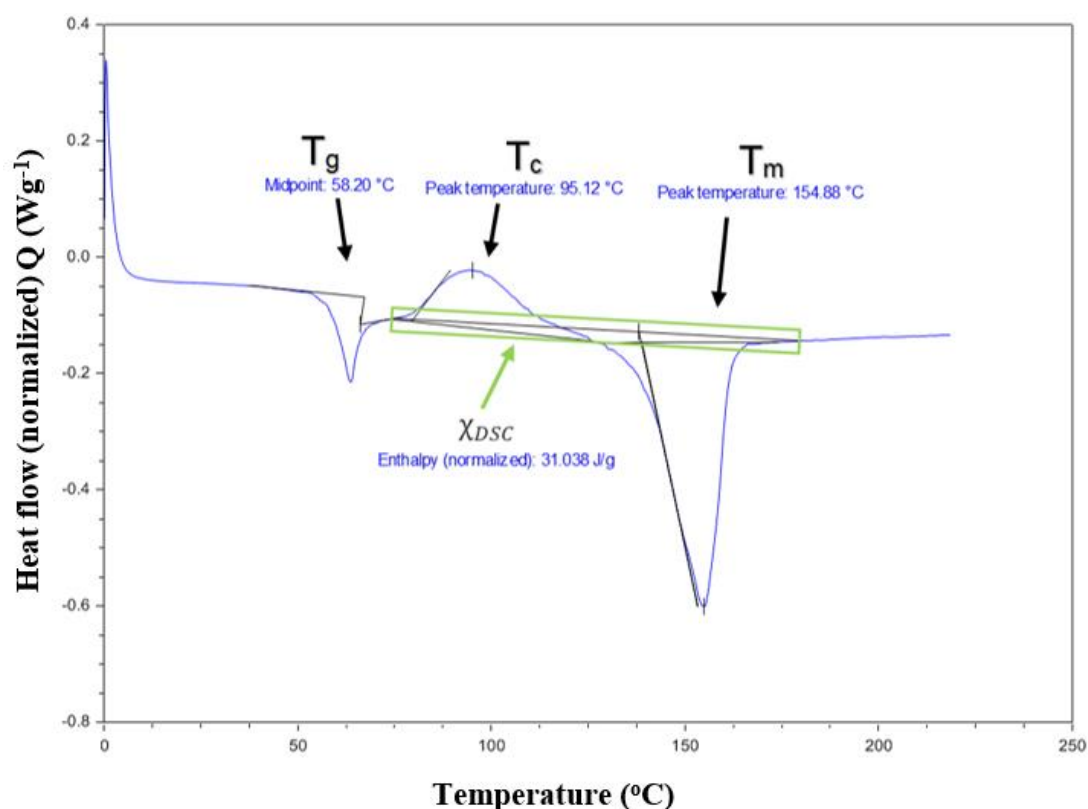


Figure 3.5: Example of heat flow temperature for PLA carried by the DSC.

3.4.3 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was used to study the thermal stability of PLA pellets and films using a TGA model 2000 (TA Instruments, Delaware, USA). Samples were placed in platinum pans and the tests were performed in a nitrogen gas atmosphere with a flowrate of 30ml/min. TGA samples were run from room temperature up to a

temperature of 600°C at an increasing rate of 10°C/min. TGA data was analysed through the usage of TA Instruments' Universal Analysis 2000 software.

Starting from decomposition temperature, both the sample stability at 5% weight loss and the degradation temperature at 50% weight loss (T_d) were calculated from TGA data. According to Figure 3.6, the decomposition of PLA starts to happen significantly at about 5% weight loss. Therefore for analytical consistency, the point at which 5% weight loss occurs will be considered and evaluated as the reference point for thermal stability. Furthermore, T_d refers to the destabilisation of a sample at 50% loss of mass (Akindoyo *et al.*, 2017).

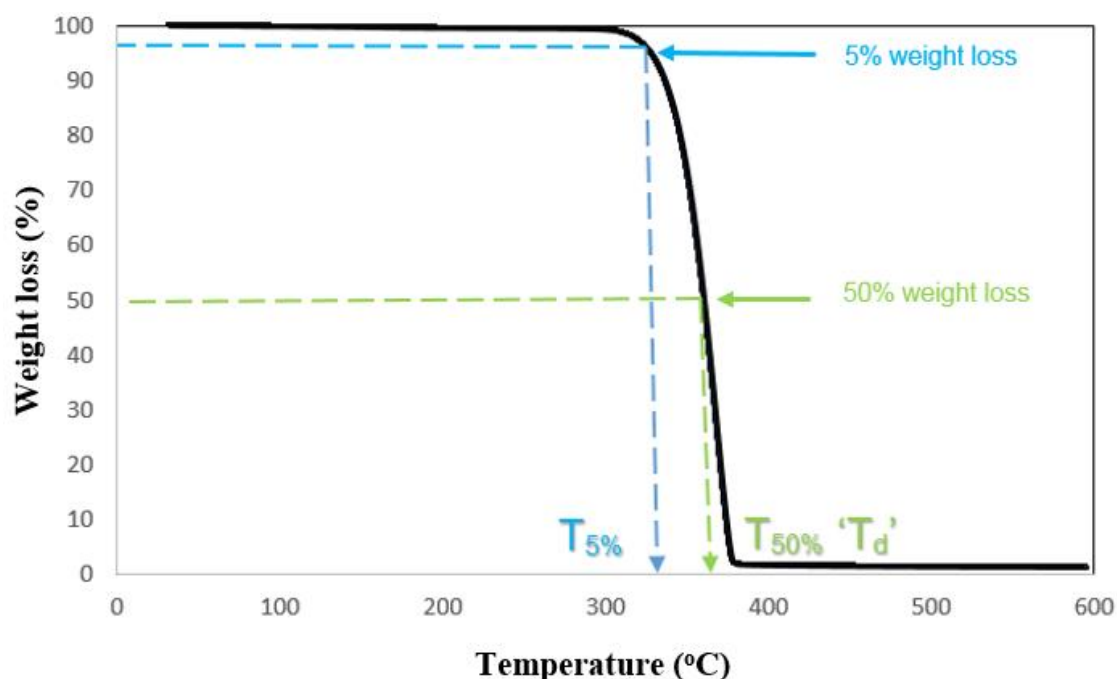


Figure 3.6: Example of a thermogravimetric measurement of PLA obtained by TGA.

3.4.4 X-ray diffraction (XRD)

X-ray diffraction (XRD) is technique used to study the crystal structure of different materials. Crystalline atoms cause a beam of incident X-rays to diffract into many directions. For these diffracted beams, their respective angles and intensities can be measured. A graphical result can then be produced showing the intensity as a function

of the angle. The shape of peaks obtained from the aforementioned graphical results can demonstrate the crystallinity of a material. A large, wide single peak denotes that a material is amorphous while a fully crystalline material would show multiple narrow peaks. For a semi-crystalline material, a combination of both wide and narrow peaks can be observed. XRD was used to observe the crystal structure of PLA and MOFs themselves as well to study the effect of the addition of MOFs particles on the crystal structure of PLA as shown in Figure 3.7. In addition, it was also used to confirm and validate the presence of MOFs in the PLA/MOFs films. All the measurements were taken at room temperature. The angle was varied from 5° to 70° in step intervals of 0.05° at a rate of 2 seconds/step. The voltage and current used were 40kV and 25mA respectively. The XRD instrument model used was a Siemens D500 diffractometer (Bruker AXS, Germany).

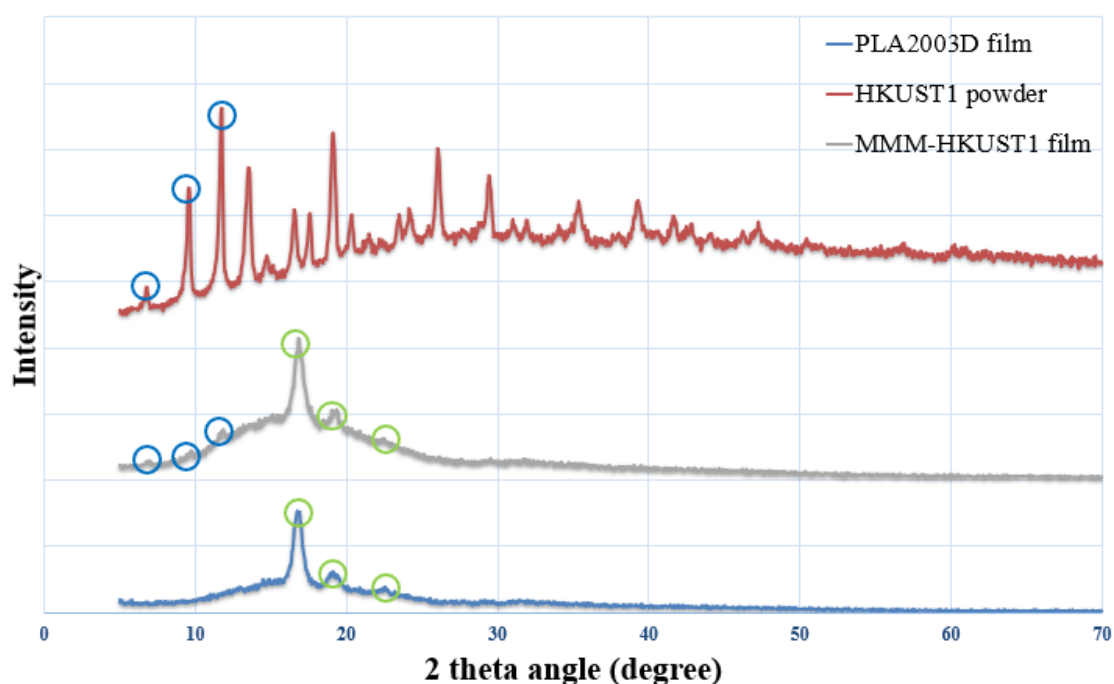


Figure 3.7: Examples of crystal-structure peaks of PLA and MMM-PLA/HKUST-1 films obtained via the XRD.

3.4.5 Gel permeation chromatography (GPC)

Gel permeation chromatography (GPC) was used to study the molecular weight of PLA polymers, and to explore varying different fabrication conditions and techniques for PLA films. The runtime and flowrate were 25min and 1ml/min respectively. Samples were prepared for GPC tests by dissolving 1mg of the sample into 1ml tetrahydrofuran (THF) solvent. The solution was then filtered through a PTFE filter with a filter size of 0.45 μ m to remove any contamination and/or undissolved PLA. The filtered solution was filled in the HPLC valves before being placed in the GPC instrument for testing.

The instrument was calibrated with PLA standard materials. The number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (PDI) for each sample was obtained using GPC and analysed using the same software.

M_n represents the number average molecular weight of the polymer chains. M_n is the total weight of all polymer molecules divided by the total number of polymer chains. For M_n smaller polymer chains are considered to be as important as bigger chains. However for M_w , the bigger molecules/chains are considered to be more important as they contain more of the total mass of the polymer sample in comparison to smaller molecules. Therefore, M_w takes into account the contribution of each polymer chain according to their respective size. PDI measures the broadness of the molecular weight distribution of a polymer. PDI is defined as the ratio of M_w to M_n for which the larger the PDI, the broader the overall molecular weight.

$$PDI = \frac{M_w}{M_n} \quad (3.4)$$

When PDI is equivalent to one, it is implied that all of the polymer molecules have the same length and the polymers are therefore described as monodisperse. The larger the polydispersity index, the wider the molecular weight distribution.

3.4.6 Thickness, density and porosity measurements

The mass, thickness, volume, density and porosity of fabricated PLA films were measured and calculated to explore their respective physical properties that were fabricated under various different conditions and parameters. A dry sample with a dimension of 3cm × 3cm was cut from each film using a sharp blade and then weighed on an electronic scale. The thickness of each sample was measured using the digital RTG-ISO23529 Rubber Thickness Gauge shown in Figure 3.8. The average of 5 measurements was recorded for each sample.



Figure 3.8: RTG-ISO23529 Rubber Thickness Gauge.

The volume was calculated by multiplying the sample area by thickness. The volume of the film can be calculated using Equation 3.5 while the porosity can be determined using Equations 3.5 – 3.7. The symbols in the equations are denoted as follows: V = effective film's volume, A = effective film's area, M = mass, Th = film's thickness, ρ = density and Φ = porosity. $V = V_v + V_p$; where V_v = the volume of film's pores 'voids' and V_p = the volume of polymer.

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For the calculation of the film volume:

$$V = \frac{M}{\rho} \quad (3.5)$$

For film's porosity can be calculated via the following:

$$\Phi = \frac{V_v}{V} = \frac{V - V_p}{V} \quad (3.6)$$

At this stage, it is important to determine the volume of polymer to calculate the film's porosity. The mass of porous film basically contributes and is equivalent to the polymer mass due to the pores being filled with air i.e. $M = M_p$. Density of PLA polymer is known to be 1.24 g/cm^3 (Khuenkeao *et al.*, 2016). For M_p = mass of polymer and ρ_p = density of polymer the respective volume is therefore:

$$V_p = \frac{M_p}{\rho_p} \quad (3.7)$$

Now, to determine the film porosity:

$$\Phi = 1 - \frac{V_p}{V} = 1 - \frac{\left(\frac{M_p}{\rho_p}\right)}{\left(\frac{M}{\rho}\right)} = 1 - \frac{\rho}{\rho_p} \quad (3.8)$$

In calculating porosity, the density of polymer is dependent on the material contents of the film's matrix. For instance, if the film matrix consists of pure PLA film the density of PLA is hence taken into account i.e. 1.24 g/cm^3 . In the case of MMMs, the density of MOF is taken into account by taking the ratio of weight between PLA and MOF. The density of HKUST-1 is measured to be 1.58 g/cm^3 . Considering an example for 5wt% HKUST-1 incorporated into a PLA matrix, the density is therefore $((1.24 \times 0.95) + (1.58 \times 0.05)) \approx 1.26 \text{ g/cm}^3$.

3.5 Membrane performance and durability tests

3.5.1 Mechanical test

A Linkam TST350 - Tensile Stress Testing System (Linkam Scientific Instruments Ltd., United Kingdom) as shown in Figure 3.9 was used to study the mechanical properties of the prepared films. The TST350 has the capability to operate at a wide range of temperature, tensile force, tensile speed and sample dimension.

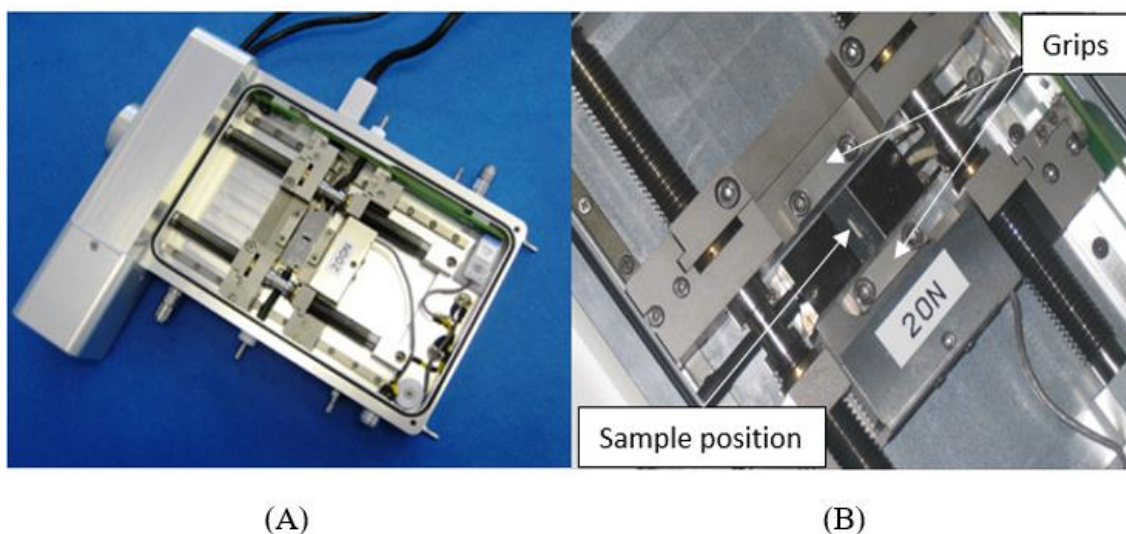


Figure 3.9: (A) TST350 tensile stress testing system and (B) specimen place in the testing system.

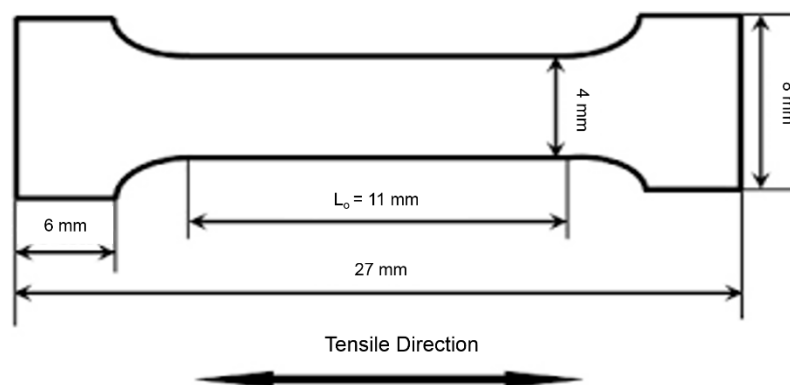


Figure 3.10: Tensile dog bone shape and its dimensions.

In experimental studies, small specimens of selected films were used to study the mechanical properties. Specimens were cut using a laser cutting machine to a dog bone shape as shown in Figure 3.10. Measurements were carried out in triplicate for each film

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specimen. Tests were conducted at room temperature and in dry conditions. Sample thicknesses were measured and the average values were reported. The specimen width and length are 4mm and 11mm respectively. In addition, the distance between grips is 15mm and the tensile speed is fixed at 0.15mm/s which corresponds to a strain rate of 0.014 per second. A 20N load cell was used as the tensile force. Stress (σ), strain (ε), Young's modulus (E) and toughness were calculated as shown in the following:

$$\sigma = \frac{F}{A} \quad (3.9)$$

$$\varepsilon = \frac{L-L_0}{L_0} \quad (3.10)$$

$$E = \frac{\sigma}{\varepsilon} \quad (3.11)$$

For which F= applied force, A_c = cross-sectional area of the test specimen (average specimen thickness $\times$ specimen width), L_0 = original length of the specimen, and L= is the length of the specimen after testing i.e. 'final length before breaking'. The calculation for modulus was considered at 1% strain. . Toughness is defined as the amount of strain energy a material can absorb before fracture occurs. Estimated calculations for toughness can be determined by considering the area under the stress-strain curve. The trapezoidal integration rule was considered to compute the film's toughness. All calculations were computed using Microsoft Excel (Microsoft Corp., USA). The table below shows an example of determined mechanical properties of a PLA film along with their respective standard deviation.

Table 3.2: An example of mechanical properties determination of a PLA film along with their respective standard deviation.

	Stress	Strain	Modulus	Toughness
	(MPa)	(-)	(MPa)	(kJ/m3)
PLA Film	1.43 ±0.06	0.11 ±0.02	39.3 ±9.8	10.26 ±1.78

3.5.2 Degradation study

PLA is a biopolymer that takes a relatively long time to degrade at room temperature. Due to the short time available to perform degradation testing, an accelerated degradation method was considered to explore the degradation behaviour of PLA. Furthermore, an accelerated degradation process at an elevated temperature was considered in order to enhance the degradation rate (Felfel *et al.*, 2016, Agrawal *et al.*, 1997).

Pure distilled water was used as the degradation medium. Degradation experiments were performed by exploring the mechanical strength behaviour of PLA films as a function of degradation time. The same shapes and dimensions of specimens used during the mechanical testing was considered in the degradation study. In addition, a similar technique using the Linkam TST350 was applied.

Specimens were placed into preheated water baths at 50°C to accelerate the degradation process. Water bath was changed regularly for every 7 days to avoid the presence of any acidic by-products that may arise during the degradation process. PLA degrades to form lactic acid. As a consequence, acidic by-products release into the water bath leading to changes in pH. Changes in pH of the surrounding environment can alter the rate of the degradation process as the hydrolysis reaction is accelerated by an acidic environment

(Agrawal *et al.*, 1997) At various time points between 1 - 7 days, three PLA film samples were taken out of the water bath and dried overnight at room temperature. The samples were then used to perform the mechanical strength test.

3.5.3 Filtration performance experimental procedures

The purpose of this experiment was to study the pure water flux (PWF) on selected membranes. In addition, some of the membranes were chosen to explore filtration performance based on solute rejections. PWF and filtration performance experiments were carried out using Koch Membrane System with a dead-end filtration cell as shown in Figure 3.11.



Figure 3.11: Koch system for membrane separation.

The effective area of the membrane was 28cm². Membranes were tested at gradual applied pressures of 2, 4, 6 and 8 bar. The permeate volume was collected and measured over a fixed time period for which the permeate was collected and measured every minute. Conducted preliminary flux tests showed that the flux started to stabilise with

less fluctuations after around 15-20 minutes as shown in Figure 3.12. Therefore, membranes were tested for 30 minutes in total to ensure that the steady state has been reached. The membrane flux was calculated using the following equation:

$$Flux = \frac{V_{cp}}{A_f \times t} \quad (3.12)$$

For which A_f : membrane effective area, V_{cp} : collected permeate volume, and t : collection duration time.

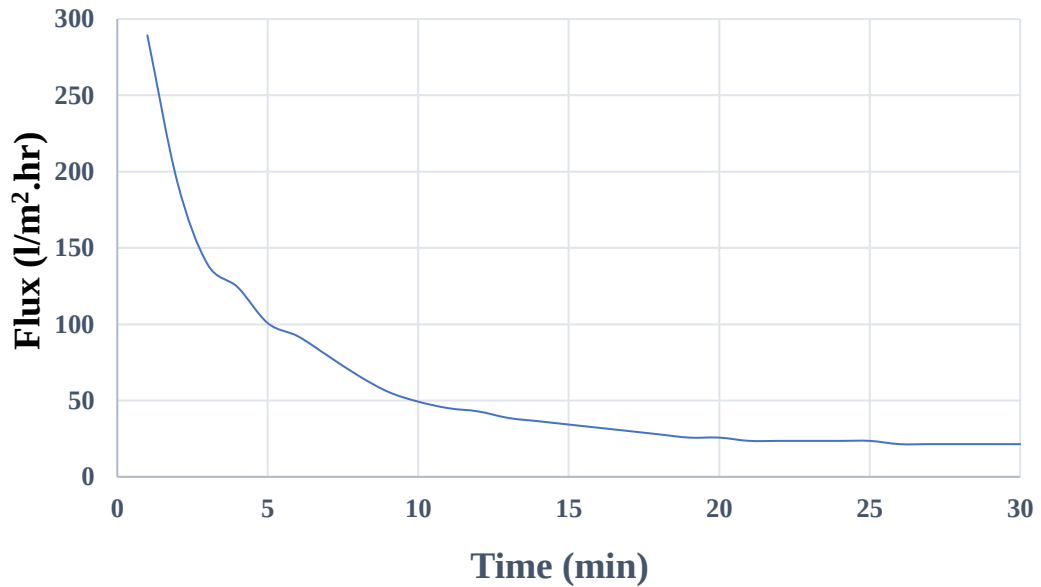


Figure 3.12: An example of flux behaviour of a PLA film.

Considering the tests for solute rejection, mixtures of solutions were prepared with a concentration of 0.5g/l (500ppm) of red dye, milk powder, ground coffee, corn flour powder and cement with a different particle sizes in distilled water. The particles size distributions of milk powder, ground coffee, corn flour, cement and red dye presented in Table 3.3.

Table 3.3: The particles size distributions of milk powder, ground coffee, corn flour, cement and red dye.

Mesh size (μm)	Particles weight distributions (%)				
	Milk powder	Coffee	Corn flour	Cement	Red dye
63<	0	0	86.7	78.7	100 (1.5 μm <)
63-125	3.4	3.6	0.5	14.8	0
125-149	3.4	2.6	0.1	0.2	0
149-177	12.6	16.4	11.7	3.7	0
177-250	46.8	14.8	0.2	0.3	0
250-420	26.3	54.5	0.1	0.2	0
>420	7.4	8.2	0.6	2.2	0

Samples of particle solutions were collected after filtration was completed. The particle concentration in the feed and permeate were then analysed using spectrophotometry UV. Solute rejections of membranes, R , were calculated using the following equation:

$$R = \left(1 - \frac{C_p}{C_f}\right) \quad (3.13)$$

For which C_p : concentration of the particle compound in permeate, C_f : concentration of particle compound in the feed (Toh *et al.*, 2007b). Table 3.4 shows an example of the efficacy of solute rejection for a PLA film after 30 minutes of separation.

Table 3.4: An example of how to calculate the efficacy of solute rejection for a PLA film after 30 minutes of separation.

	Concentration (g/l)	Rejection (%)
Feed	0.50	0.0
Permeate	0.0075	98.5

Membrane flux is defined as the rate of solvent flow through the membrane. Permeability on the other hand is the measurement of the solvent flow through a membrane. Unlike flux, permeability is normalised with respect to pressure.

$$\text{Permeability} = \frac{\text{Flux}}{\Delta P} \quad (3.14)$$

In analysing membrane solute rejection, the molecular weight cut-off (MWCO), defined as the lowest molecular weight at which greater than 90% of a solute with a known molecular weight is retained by the membrane, is measured (Cassano *et al.*, 2018). Membrane rejection is the measurement in regards to the selectivity of a membrane for a particular compound (Biesheuvel *et al.*, 2019). Selectivity is directed by the surface properties of membranes that determine the type of compounds that can pass through. Whereas flux describes the transportation rate at which compounds pass through the membrane.

Essentially, membranes selectively reject solutes based on their pore size whereby large molecules are retained and smaller molecules are allowed to pass through. In general, membranes with low fluxes have high rejections and vice versa (Toh *et al.*, 2007a). The design of membranes are often a trade-off between flux and rejection.

Chapter 4: Establishing Fabrication Conditions of Porous PLA Films

4.1 Introduction

Petroleum derived polymers such as polystyrene, polypropylene, polyethylene and polyethylene terephthalate have been widely used for various industrial applications. However, they are considered to be unsustainable and environmentally harmful substances as they produce undesirable waste products that also release hazardous gases during decomposition (Weber *et al.*, 2002, Khuenkeao *et al.*, 2016). To overcome these challenges, bio-based polymers have become an interesting and alternative field of research. Biopolymers are mainly extracted from biomass of i.e. vegetable oil, sugar or synthesised from bio-derived monomers such as starch, bacteria and cellulose (Weber *et al.*, 2002, Mohan *et al.*, 2016). Biopolymers have attained excessive interest and commercial significance in the last decade. Examples of well-known biopolymers include chitosan, polylactic acid and cellulose (Bakar and Tan, 2016).

One of the most common and commercially popular biopolymers is the PLA. PLA is the most widely utilised, investigated and promising biopolymer due to its numerous as well as unique advantages over other polymers. In addition, PLA is the second most produced biopolymer after starch-based biomaterials (Kalia and Avérous, 2011). Production of PLA is eco-friendly, biocompatible, easy-to-process and energy efficient (Farah *et al.*, 2016). Moreover, PLA can also be produced from non-toxic, renewable feedstock in addition to being a naturally occurring organic acid (Lasprilla *et al.*, 2012). In addition to being derived from renewable sources, PLA is also considered to be biodegradable, compostable, eco-friendly and recyclable in nature (Drumright *et al.*, 2000, Sawyer, 2003).

Chapter 4: Establishing Fabrication Conditions of Porous PLA Films

Utilisation of a more biodegradable polymeric matrix such as PLA films can work towards justifying and mitigating some environmental concerns. Recent studies have concentrated on implementing PLA in medical applications and packaging. This chapter is focussed on establishing the conditions and parameters to fabricate novel uniform porous PLA films. Establishing conditions for film preparation with pure, dried and melted PLA polymer pellets by investigating the effect of a non-solvent bath and the concentration of PLA were considered. In addition, the influence of the drying technique, type of casting substrate and casting thickness were also studied. XRD was used to detect the crystal structure of the PLA films. The top side and cross-sectional SEM images were used to study the morphology of films. Thermal properties and chemical/thermal stability of polymer pellets and films were explored using DSC and TGA. Physical properties such as density, mass, porosity and final thickness of the fabricated films at varying casting thicknesses were measured.

4.2 Pre-treatment effects on PLA pellets

4.2.1 Thermal properties

The thermal properties of pure, dried and melted PLA polymer pellets was studied using DSC and is summarised in Table 4.1. Each sample was initially heated to 220°C to erase any prior thermal history before being immediately cooled down to 0°C. Subsequently, the sample was once again heated to 220 °C to observe any changes in thermal properties. The behaviour of pure, dried and melted PLA pellets after the second heating are shown in Figure 4.1. The heat flow behaviour has been explained in detail in Section 3.4.2, where the first change in heat flow typically indicates T_g followed by T_c and then the final heat flow change associated with T_m . The thermal properties of PLA pellets were analysed based on the second heating and is summarised in Table 4.1. The values

of T_g , T_c and T_m for pure pellets were approximately calculated to be 61.2°C, 128.4°C and 156.1°C, respectively.

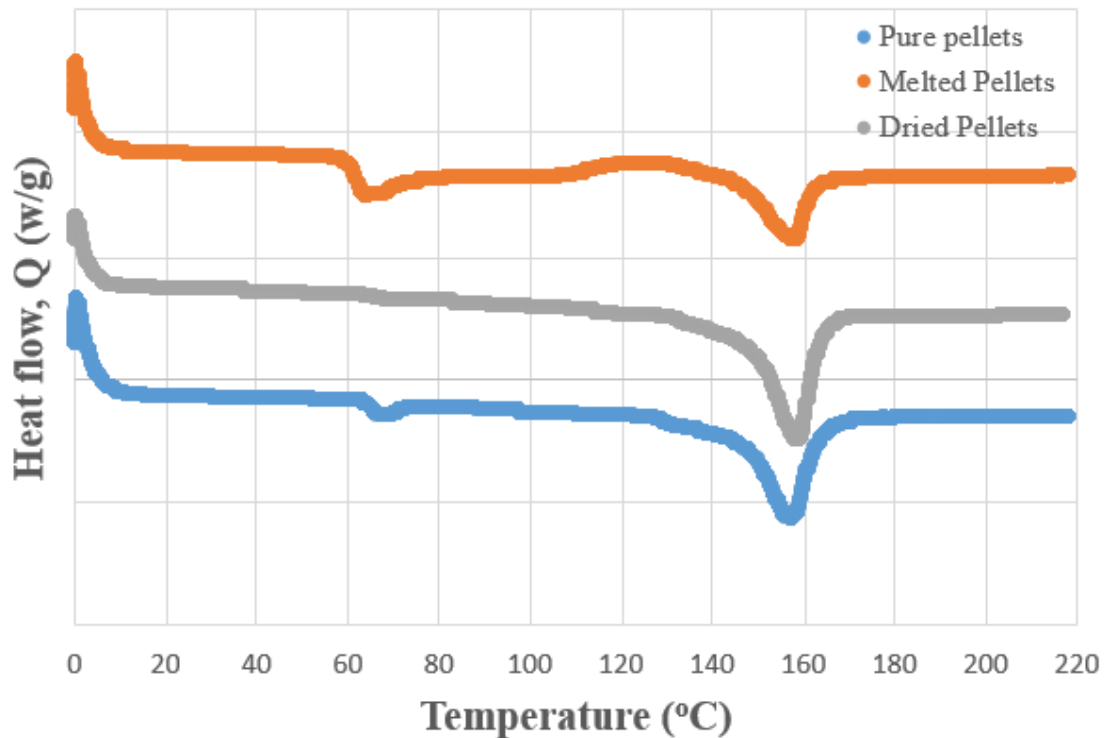


Figure 4.1: DSC curves of the second heating for pure, dried and melted PLA pellets.

Dried PLA pellets had slightly reduced T_g , T_c and T_m with the values being 60.8°C, 127.9°C and 156°C, respectively. In addition, the crystallinity of dried pellets reduced to 1.6% from 2.7% for pure pellets. For melted pellets, the T_g value and crystallinity decreased down to 60.2°C and 1.5%, respectively. These findings are in agreement to the study performed by Zhang *et al.* (2012) that reported the PLA exhibits poor crystallinity compared to other materials. The crystallinity of PLA was found to be typically less than 10%. On the other hand, T_c and T_m values of melted pellets slightly increased to 130.5°C and 156.3°C respectively. Small changes in the thermal properties of dried and melted pellets compared to pure pellets suggest that drying or melting PLA pellets has no significant effect on the thermal properties of PLA pellets. Furthermore, DSC results showed that drying and melting PLA pellets reduced T_g and the crystallinity of PLA polymer.

Table 4.1: Thermal properties of pure, dried and melted PLA pellets obtained from second heating.

	T_g (°C)	T_c (°C)	T_m (°C)	χ_{DSC} (%)
Pure Pellets	61.2	128.4	156.1	2.7
Dried Pellets	60.8	127.9	156.0	1.6
Melted Pellets	60.2	130.5	156.3	1.5

The results for the thermal properties of pure PLA pellets are in agreement with available data in previous literature and are compared in Table 4.2.

Table 4.2: Comparison of thermal properties of pure PLA pellets in this study and other studies.

	T_g (°C)	T_c (°C)	T_m (°C)	χ_{DSC} (%)
This study	61.2	128.4	156.1	2.7
(Tee <i>et al.</i>, 2013)	59.0	113.0	158.0	9.0
(Fehri <i>et al.</i>, 2016)	59.4	108.8	154.0	5.6
(Khuenkeao <i>et al.</i>, 2016)	59.5	128.1	151.0	1.4

4.2.2 Thermal stability

The thermal stability of pure, dried and melted PLA pellets were studied using TGA. Trends for all the different types of PLA pellet samples are similar with only one step of mass loss as shown in Figure 4.3. The weight loss due to the degradation of samples took place between 300°C and 380°C. As seen from Figure 4.2, the decomposition of PLA begins to occur at a faster rate at around 5% weight loss. Therefore for analytical consistency, the point at which 5% weight loss occurs will be considered and evaluated as the reference point for thermal stability. Thermal stability at 5% weight loss of the pure pellets was evaluated to be 329°C.

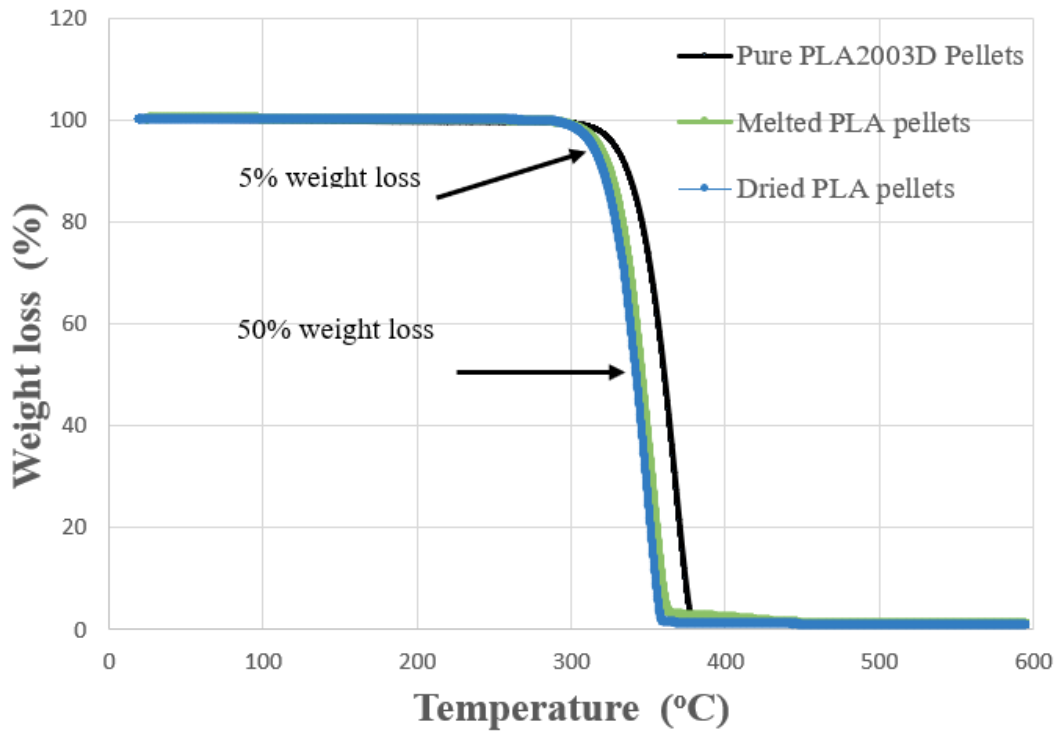


Figure 4.2: Thermal stability of pure, dried and melted PLA pellets.

The stability at 5% weight loss of the dried and melted pellets shifted to 314°C and 318°C respectively. This result is in agreement with Tee *et al.* (2013) who reported that PLA had only one step in weight loss with degradation temperatures ranging from 316°C to 372°C. Furthermore, Kim *et al.* (2008) showed that PLA polymer degrades between 300°C and 400°C.

The degradation temperature (T_d) is considered when 50% weight loss of a sample occurs thus also indicating destabilisation (Akindoyo *et al.*, 2017). The T_d for different samples is shown in Table 4.3. Pure pellets has a T_d value of 361°C, whereas the value for T_d shifted to 343°C and 346°C for dried and melted pellets respectively. By considering the residual weight at 600°C for all the samples, nearly the same amount of residue was left which ranges from 0.78% to 1.19% among all the samples. No weight loss was observed for all the samples prior to degradation testing thus indicating that the polymer pellets were entirely dry with no other components or contamination (water/

moisture) at $\approx 100^\circ\text{C}$. In conclusion, TGA results confirm that either drying or melting pellets do not actually improve the thermal stability of PLA polymer. In fact, TGA results show that pure pellets start to decompose at higher temperatures while also exhibiting higher thermal stability and degradation temperatures compared to dried and melted PLA pellets.

Table 4.3: TGA results of pure, dried and melted PLA pellets.

	5% weight loss ($^\circ\text{C}$)	50% weight loss, T_d ($^\circ\text{C}$)	Residue at 600 $^\circ\text{C}$ (%)
Pure pellets	329	361	1.10
Dried pellets	314	343	0.78
Melted pellets	318	346	1.19

4.2.3 Molecular weight analysis

M_n , M_w and PDI of pure, dried and melted PLA pellets were measured using GPC (Table 4.4). Pure PLA pellets showed the highest molecular weights with values of $M_n \approx 90.7\text{kDa}$ and $M_w \approx 162.6\text{kDa}$. Compared to pure pellets, both dried and melted pellets showed lower molecular weights. This confirms clearly that drying and melting pellets in advance effects the molecular weight of the resulting PLA pellets.

Table 4.4: M_n , M_w and PDI of pure, dried and melted PLA pellets.

	M_n (kDa)	M_w (kDa)	PDI
Pure Pellets	90.7	162.6	1.8
Dried Pellets	81.8	149.8	1.8
Melted Pellets	78.5	138.3	1.8

Low M_n values for dried pellets indicate that polymer chains break down to sub-chains during the drying of pellets thus resulting in lower average molecular weights (81.8kDa) compared to pure pellets (90.7kDa). This may occur since the pellets were dried at

100°C which is above the T_g value for PLA ($\approx 64^\circ\text{C}$). As a result of this, the polymer chains started to break down into smaller chains. Another possible reason could be that polymer started to degrade more slowly as the PLA pellets were dried at a high temperature (100°C). This is confirmed by the lower M_w value for dried pellets (149.8kDa) compared to pure pellets (162.6kDa). Melted pellets exhibited the lowest values for M_n and M_w among all the samples. Most probably, the low value of M_w for melted PLA (138.3kDa) was due to the heating of PLA pellets at a very high temperature (220°C). It appears that heating the PLA pellets at 220°C led to degradation of PLA. According to the results obtained from GPC analysis, drying and melting PLA pellets reduced their molecular weights with pure PLA pellets exhibiting both higher number and weight average molecular weights. In agreement with the results of GPC analysis, TGA confirmed that pure PLA pellets had higher thermal stability compared to dried and melted pellets.

4.3 Fabrication of porous flat sheet PLA films via casting and solvent-nonsolvent exchange.

4.3.1 Establishing PLA concentrations

PLA polymer films were prepared by dissolving PLA pellets in DMSO solvent and mixing them at 80°C for 24 hours. After casting films with an initial thickness of 150 μm on a glass substrate, the casted films along with the substrate were immersed in a 25°C water bath for 24 hours. Resulting films were dried in an oven at 25°C for 24 hours. PLA films were prepared with PLA concentrations of 2.5, 5, 10, 15 and 20 percent by weight. PLA/DMSO ratios were selected based on the molecular weights of PLA as discussed in Section 3.3 in the chapter for Materials and Methodology.

It was easier to control the casting of films prepared at PLA weight concentrations of 5%, 10% and 15% in comparison to PLA concentrations of 2.5% and 20% due to the viscosity of the mixture. It was observed that for a PLA concentration of 2.5%, the viscosity of the mixture was low allowing for the thickness of the casting to be controlled. On the other hand, casting was difficult to be controlled at high viscosities. More particularly, when the polymer/solvent ratio was increased to 15% and 20%, the polymer mixture became more viscous resulting in difficult film casting. It shall be noted here that even a small increase in the concentration of the polymer, i.e. from 10% to 15%, has instigated changes in the viscosity of the mixture. Films prepared with higher polymer concentrations (15% and 20wt%) were found to be irregular and non-uniform with teared sections and breakage (Figure 4.3). In fact, after the PLA/DMSO solvent mixture was poured into the glass substrate and exposed to air, the resulting mixture solidified within a couple of seconds. At those polymer concentrations, the formation of flat continuous films were not achieved. This may have occurred due to some undissolved polymer chains, probably long chains, due to the high percentage of polymer in the mixture solution which subsequently prevented successful film formations. Therefore, increasing the mixing time and/or increasing the amount of solvent may result in the formation of continuous and uniform films. By increasing the amount of solvent, uniform and continuous PLA film structures were formed with 5% and 10% PLA concentrations as shown in Figure 4.3. Solution viscosity was medium for ratio 10/90 and relatively low at 5/95 ratio.

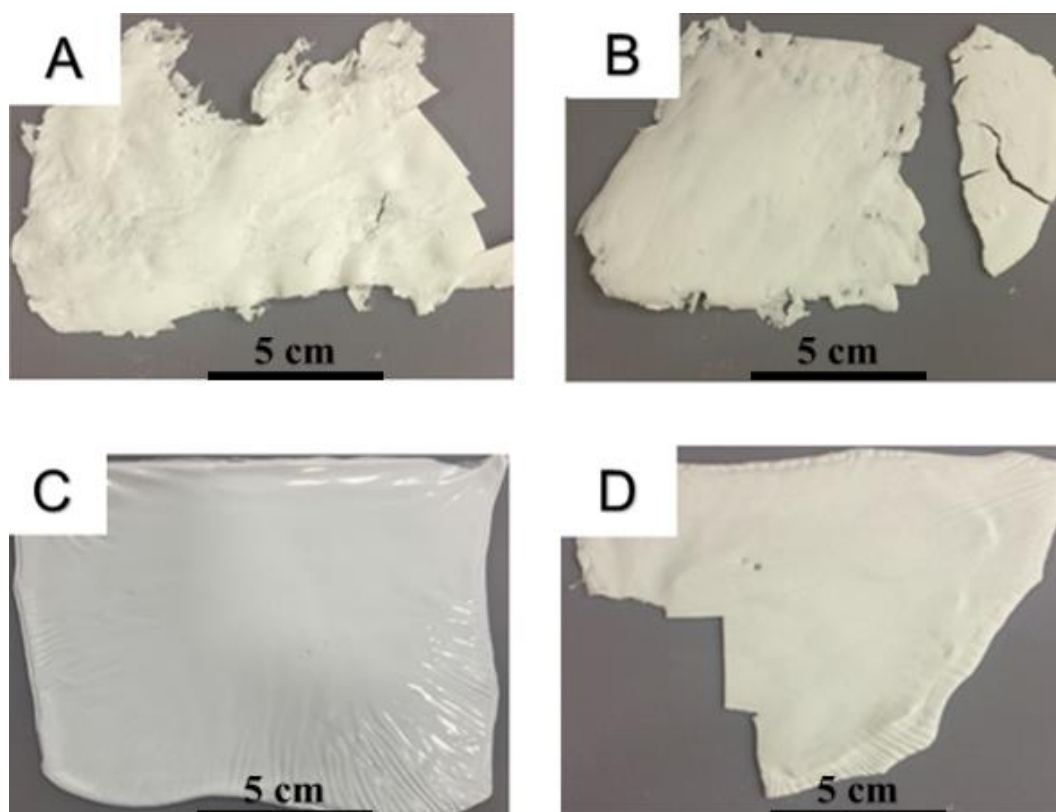


Figure 4.3: Surface morphological structure (Top side) of 150µm thick PLA films casted on glass substrates prepared at various PLA concentrations. PLA films prepared using PLA/DMSO ratios of; (A) 20/80, (B) 15/85, (C) 10/90 and (D) 5/95. Non-solvent bath=water. Mixing at 80 °C for 24hours, immersion in non-solvent bath at 25 °C for 24 hours, and film drying in an oven at 25 °C for 24 hours.

SEM images of PLA films prepared with 15/85 and 20/80 polymer/solvent ratios are shown in Figure 4.4. The top view SEM images of the top surface layer of films show that the films prepared exhibited no pores started or completed. Cross-sectional images showed pore channels were formed for films prepared with 15/85 polymer/solvent ratio while no channels were formed for films prepared with 20/80 polymer/solvent ratio. The thickness of the top and bottom regions are approximately 50µm and 650µm for films prepared with 15/85 polymer/solvent ratio respectively. On the other hand, the thickness of the top and bottom regions were determined to be 70µm and 350µm for films prepared with 20/80 polymer/solvent ratio respectively. The top surface and cross-sectional SEM images (Figure 4.5-A2 & B2) show that the films exhibit small spherical particles (most probably polymer) positioned beside each other. The particles indicate

that the polymers that did not fully dissolve in the solvent or that DMSO did not have their phases fully exchanged with water in the non-solvent bath. In addition, these particles may also be crystallised polymers that could not dissolve in the solvent.

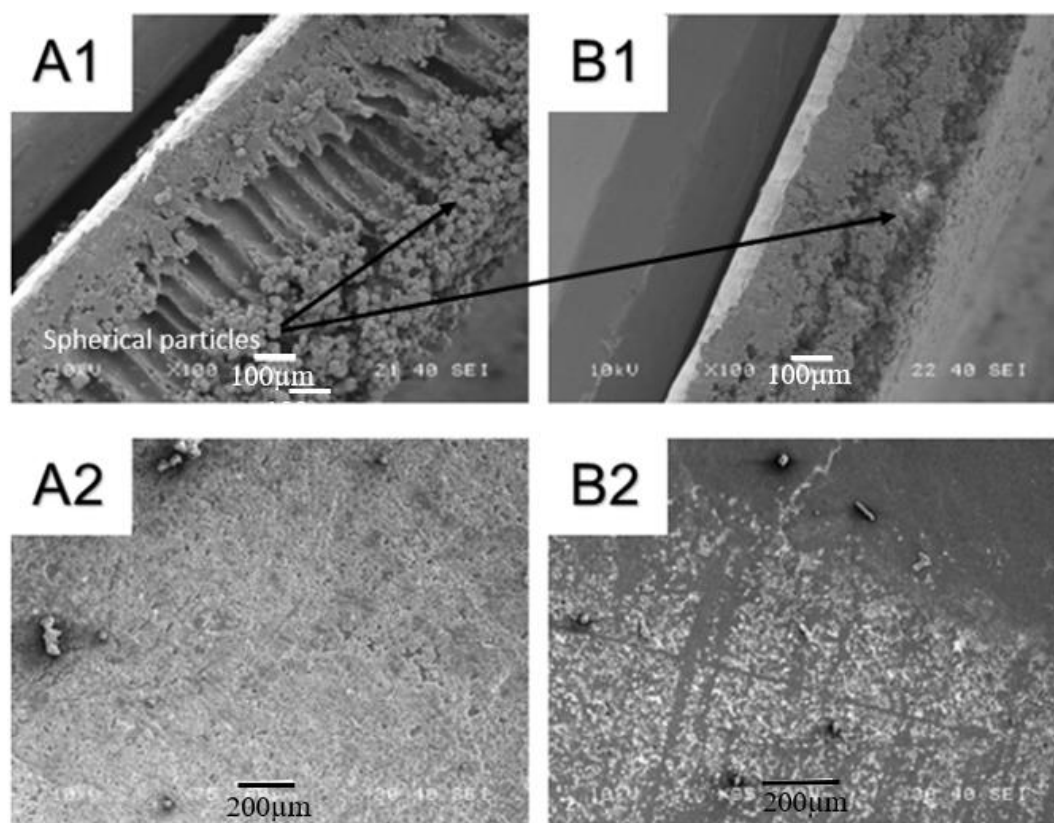


Figure 4.4: Top view and cross-sectional SEM images of PLA films using PLA/DMSO ratios of 15/85 (A1, A2) and 20/80 (B1, B2). Non-solvent bath=water. Mixing at 80 °C for 24hours, immersion in non-solvent bath at 25 °C for 24 hours, and film drying in an oven at 25 °C for 24 hours.

In increasing the amount of solvent, PLA films prepared using PLA/DMSO ratios of 5/95 and 10/90 were also studied (Figure 4.5). Considering the SEM images taken for both ratios, film structures were shown to be relatively uniform and continuous. With the presence of pores, films prepared using PLA/DMSO ratios of both 5/95 and 10/90 show some potential to be used as membranes. In regards to the thickness of films, the SEM images show that the film prepared with the 5/95 ratio has relatively higher total thickness compared to that of the film prepared with the 10/90 ratio. The thickness of the top and bottom regions for both films are approximately 20µm and 550µm respectively.

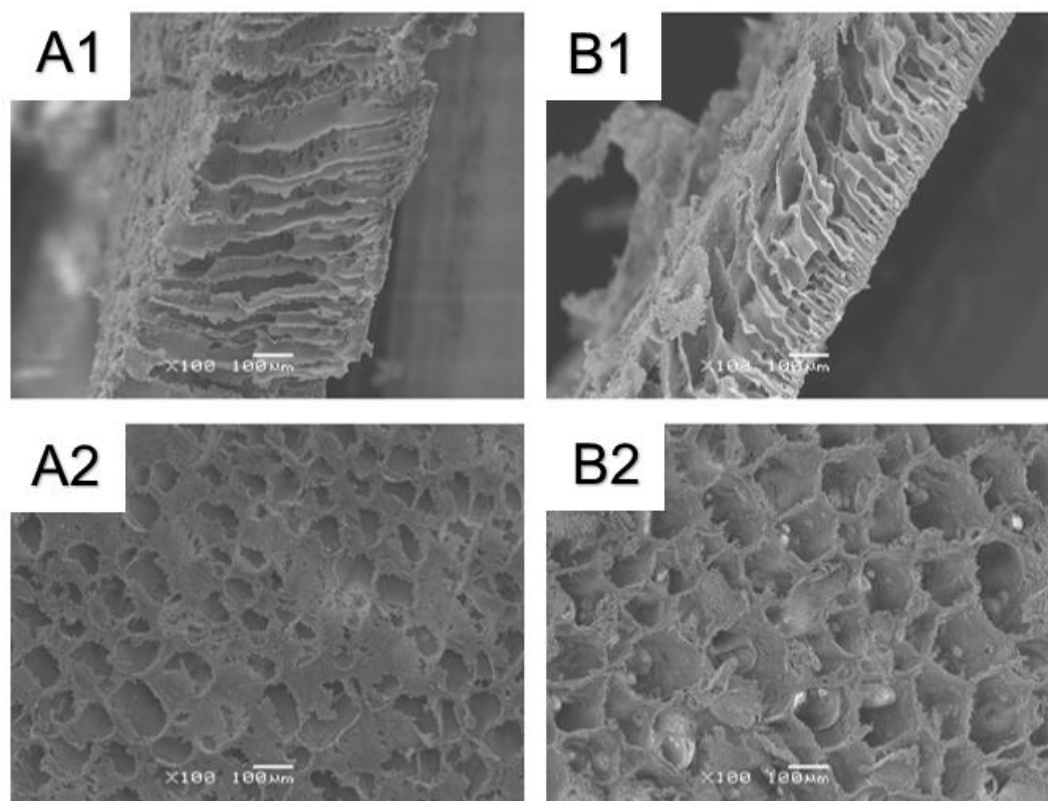


Figure 4.5: Top view and cross-sectional SEM images of PLA films using PLA/DMSO ratios of 5/95 (A1, A2) and 10/90 (B1, B2). Non-solvent bath=water. Mixing at 80 °C for 24 hours, immersion in non-solvent bath at 25 °C for 24 hours, and film drying in an oven at 25 °C for 24 hours.

According to the above results, it can be concluded that films prepared with PLA concentrations of 5% and 10% have the potential to be selected for porous membrane applications. The top and cross-sectional SEM images confirmed their porosity. In addition to being porous, films formed at both of these concentrations were also found to be continuous. Despite this, it is important to note that the films did exhibit some surface tension/stress due to shrinkage. This will be further investigated and discussed in Sections 4.2.2.2 and 4.2.2.6.

4.3.2 The effect of substrate type

After PLA films were cast onto glass substrates, some of the films immediately showed shrinkages after they were immersed in the non-solvent bath. Teflon substrates were proposed to be used instead of glass substrates due to the nature of Teflon which is non sticky. Teflon is also widely used as a casting substrate for membrane formation. Hence,

Teflon substrates were used to mitigate the shrinking of films. No shrinking was observed in preparing films using Teflon substrates. However, it was observed that the usage of Teflon substrates led to the precipitation of some PLA powders underneath the film as shown in Figure 4.6. The same observation was made throughout more than five experiments in using the aforementioned substrates to prepare films. It was also observed that the films did not leave the substrate and that only the top side of the films were formed. This is most likely due to the absence of solvent and non-solvent phase exchange. In addition, Teflon substrate is hydrophobic while glass is hydrophilic (Linares *et al.*, 2017). Hence, using Teflon substrates would possibly lead to the prevention of water flow from the top side of the film to the bottom side and subsequently diffusion with DMSO. As a results of this, it was decided for glass substrates to be used as casting substrates for PLA film fabrication. Film structure and surface tension ‘shrinkage’ issues will be expanded and discussed further in this chapter, Section 4.2.2.6.

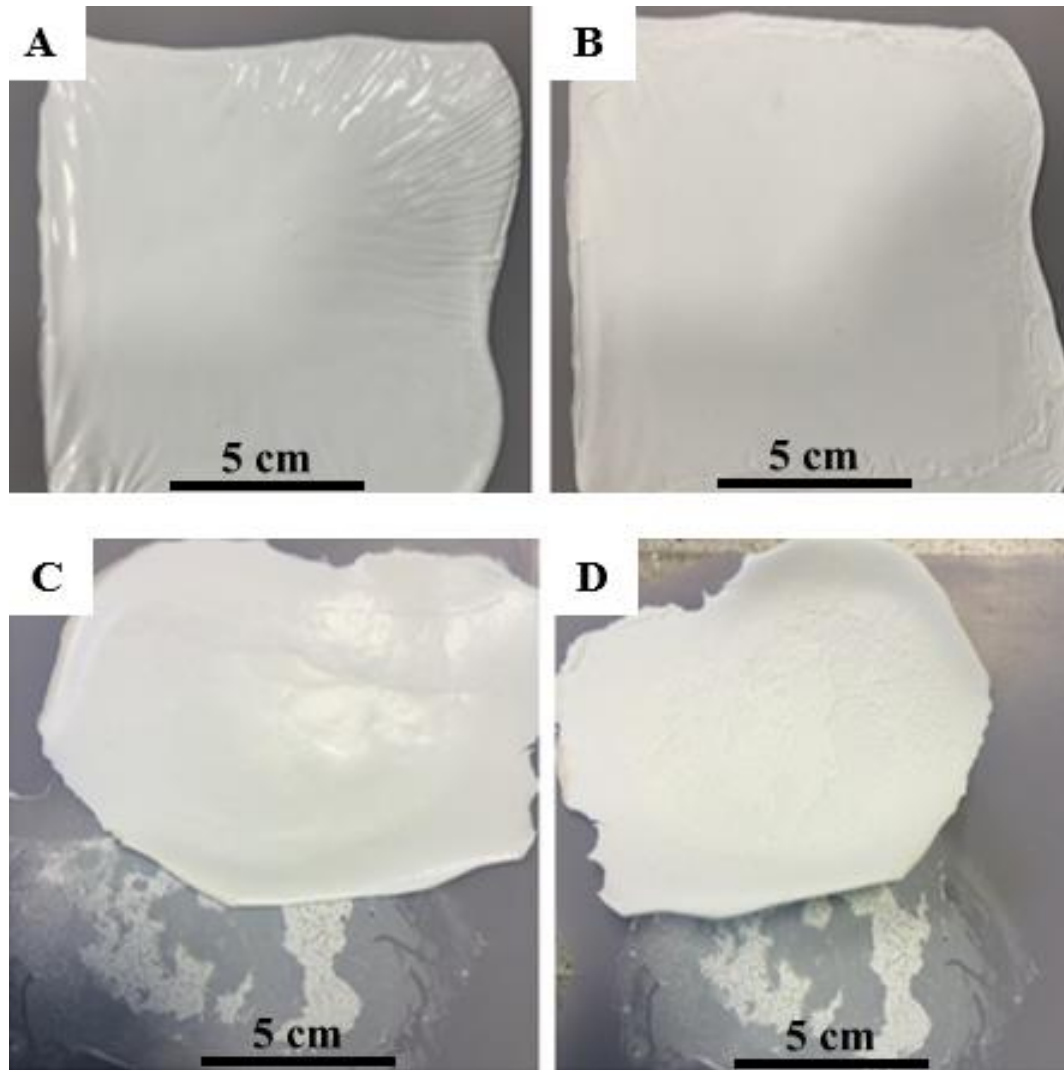


Figure 4.6: Top and bottom sides of the fabricated PLA films casted on (A) glass substrate ‘Top side’, (B) glass substrate ‘bottom side’ and (C) Teflon substrate ‘Top side’, (D) Teflon substrate ‘bottom side’.

4.3.3 The effect of non-solvent bath

After establishing the PLA film concentrations and selecting the casting substrate, 5% PLA concentration was selected to explore the influence of the type of solvent used in non-solvent bath for the fabrication of untreated (pure pellets) and treated (dried and melted pellets) PLA films. So far, only water has been used in the non-solvent bath. The main objective of this investigation was to determine the best type of raw PLA pellets that produces the most successful film in terms of surface structure, micro-morphology, thermal properties and thermal stability in relation to the non-solvent bath.

Water, methanol (MeOH) and 50/50 v/v% mixture of water/methanol were used as a non-solvent bath for a polymer/solvent ratio of 5/95. When pure MeOH was used as the non-solvent bath, the films produced exhibited tears and did not properly form during the immersion step even after 24 hours. This is presented in Figure 4.7. Similar observations were made when the experiment was performed using treated and untreated pellets. This may suggest that phase exchange between DMSO and MeOH did not occur. Another possible reason is that MeOH is a poor non-solvent for PLA and thus did not facilitate phase inversion. Films were successfully fabricated implementing pure water and 50/50 water/MeOH non-solvent baths for both treated and untreated pellets. However, films prepared from melted pellets were determined to be more brittle than the ones prepared from pure or dried pellets. Their surface structure was also found to be less uniform in nature.

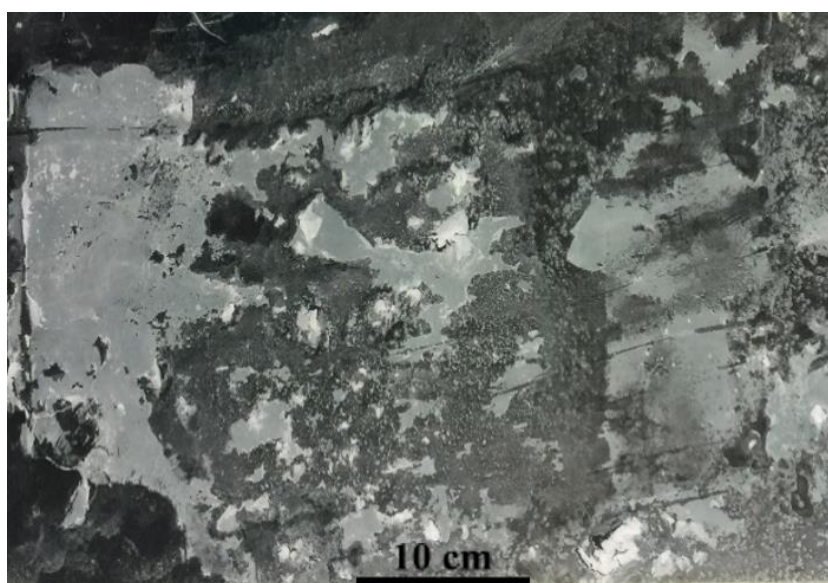


Figure 4.7: Optical surface structure of PLA film prepared from pure PLA pellets and immersed in pure MeOH bath.

SEM images of PLA films prepared from pure pellets at a PLA concentration of 5wt% with a non-solvent bath consisting of water and 50/50% water/MeOH are shown in Figure 4.9. Films prepared with both water and 50/50% water/MeOH exhibited similar patterns of dense or low porous top layers. In the cross-sectional images, the formation

of macro-void channels with finger-like structures were observed. Films immersed in a water bath has an approximate top layer thickness of 20 μ m and a bottom layer thickness of 550 μ m. Considering the film immersed in 50/50% water/MeOH non-solvent bath, the film thickness was estimated to be around 15 μ m and 650 μ m for the top and bottom layer respectively.

As mentioned previously, SEM cross-sectional images for films prepared from both non-solvent baths show the formation of finger-like structures on the top region. Solid aggregates of polymer can be observed in the bottom region. Domingues *et al.* (2016) has reported that the formation of the morphological structure of PLA films due to phase inversion via the precipitation technique is the result of a complex set of interactions between the polymer, solvent and non-solvent. The precipitation velocity follows a complex thermodynamic pathway resulting in different precipitation mechanisms occurring at the top and bottom layers of the flat sheet films. Supposedly, faster precipitation occurs at the top region while a lower precipitation velocity is seen at the bottom layer. With the top layer already being formed, it acts as a resistance against the mass transfer of the solvent and non-solvent to the bottom layer. This delays the phase exchange in the bottom layer thus making it a polymer-rich phase. Films immersed in 50/50% water/MeOH non-solvent bath (Figure 4.8 -B1 and Figure 4.8 -B2) showed a more polymer-rich phase with more polymer aggregation and less continuous pore channels compared to films immersed in a water bath (Figure 4.8 -A1 and Figure 4.8 -A2). Furthermore, SEM images showing the top view confirmed that the prepared films exhibited both non-uniform and non-homogenous pore sizes (Figure 4.8 -A1 and Figure 4.8 -B1).

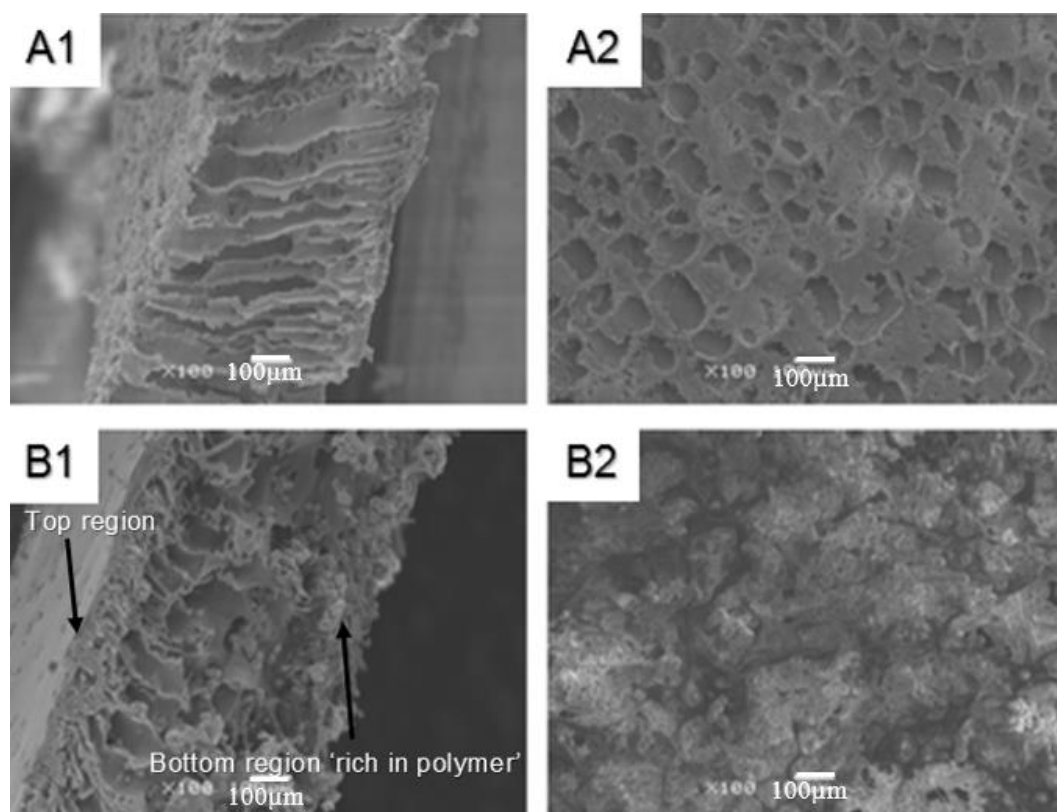


Figure 4.8: Top view and cross-sectional SEM images of PLA films prepared from pure PLA, and immersed in various non-solvent baths. PLA/DMOS ratios = 5/95. (A1, A2) immersion bath type is water and (B1, B2) 50/50% water/MeOH bath. Mixing at 80 °C for 24 hours, immersion in non-solvent baths at 25 °C for 24 hours, and film drying in an oven at 25 °C for 24 hours.

SEM images of PLA films prepared from dried pellets at 5% PLA with water and 50/50% water/MeOH as non-solvent baths are shown in Figure 4.9. Both films exhibited similar patterns of dense or low porous top layers consisting of finger-like structures and sponge-like structures in the cross-sections. Both films showed nearly similar film thicknesses with the thickness of top and bottom regions measuring approximately 20µm and 340µm, respectively.

Cross-sectional images (Figure 4.9 -A1 and Figure 4.9 -B1) show the formation of finger-like structures on the top regions and the formation of solid aggregates of polymer with folded layers on the bottom region. This type of morphology is likely formed due to the different precipitation mechanisms that occur on the top and bottom layers of the films in which the top region/layer forms much quicker than the bottom region. The top

region being formed first reduces or prevents phase exchanges in the bottom region and consequently leaves the bottom region as a polymer-rich phase. Considering Figure 4.9 -A2 and Figure 4.9 -B2, it can also be seen that both films exhibited non-uniform and/or non-visible pores.

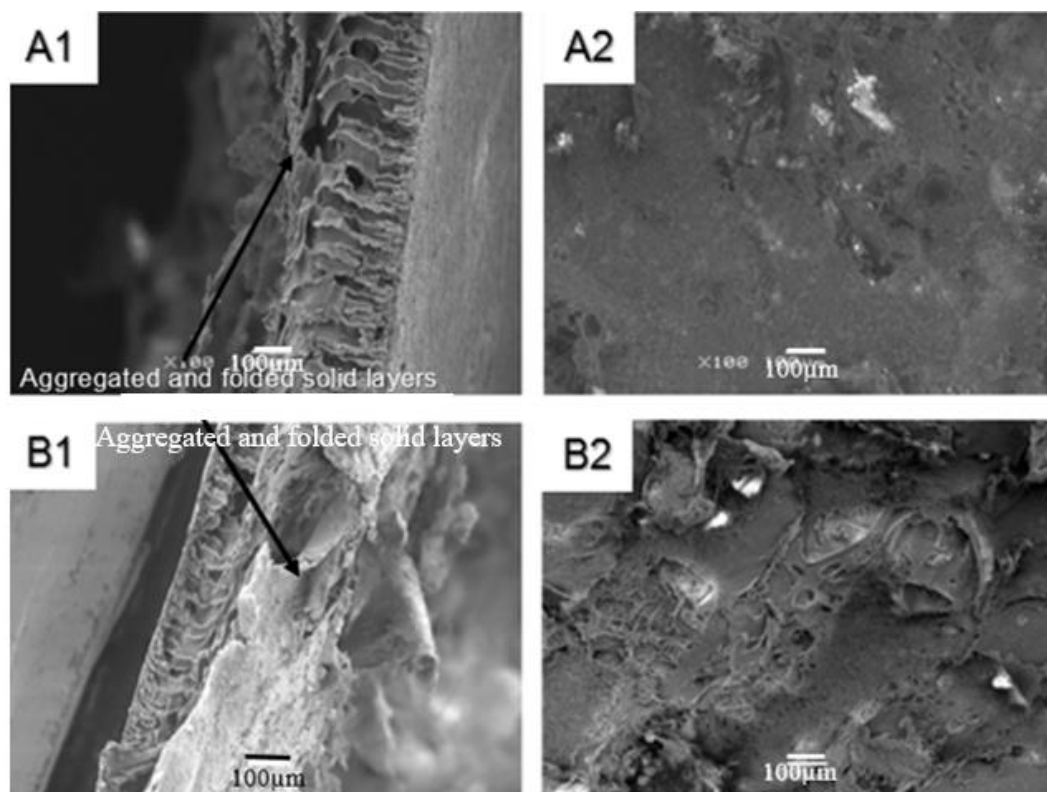


Figure 4.9: Top view and cross-sectional SEM images of PLA films prepared from dried PLA, and immersed in various non-solvent baths. PLA/DMOS ratios = 5/95. (A1, A2) immersion bath type is water and (B1, B2) 50/50% water/MeOH bath. Mixing at 80 °C for 24 hours, immersion in non-solvent baths at 25 °C for 24 hours, and film drying in an oven at 25 °C for 24 hours.

SEM images of PLA films prepared from melted pellets at 5% PLA concentration with water and 50/50% water/ MeOH as non-solvent baths are shown in Figure 4.10. Films prepared using both water and 50/50% water/MeOH non-solvent baths exhibited similar patterns of dense or low porous top layers. Considering cross-sections of the films, sponge-like structures are mainly formed along with finger-like structures. The thickness of the top and bottom regions for the film immersed in water bath are approximately 10µm and 150µm respectively. The thicknesses respectively increased to 20µm and 550µm when the film was immersed in 50/50% water/MeOH bath.

Cross-sectional images (Figure 4.10 -A1 and Figure 4.10 -B1) show the formation of macro-void channels in the top regions with sponge-like structures consisting of polymeric solid aggregates and folded layers in the bottom region. According to the SEM images, melted polymer pellets affect the morphology of the films due to a decrease in precipitation velocity thus resulting in sponge-like structures with a rich polymer phase accreting on the bottom region of the films. Considering Figure 4.11 -A2 and Figure 4.11 -B2, non-uniform and/or non-visible pores can be observed.

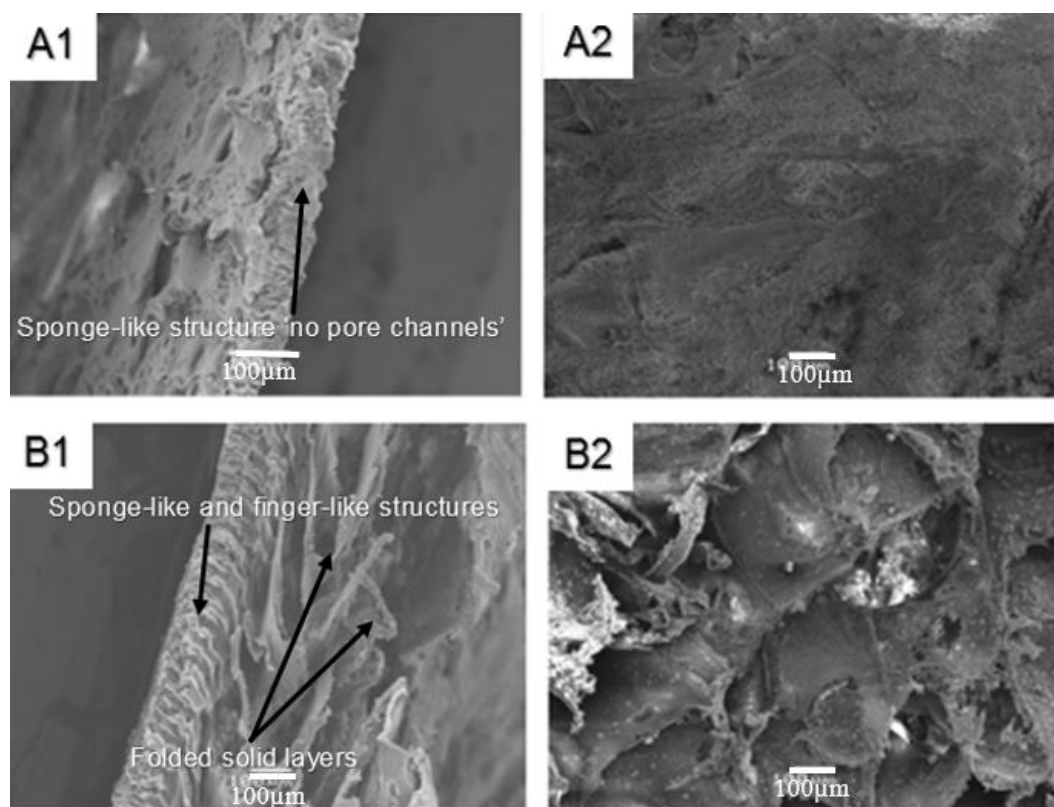


Figure 4.10: Top view and cross-sectional SEM images of PLA films prepared from melted PLA, and immersed in various non-solvent baths. PLA/DMOS ratios = 5/95. (A1, A2) immersion bath type is water and (B1, B2) 50/50% water/MeOH bath. Mixing at 80 °C for 24 hours, immersion in non-solvent baths at 25 °C for 24 hours, and film drying in an oven at 25 °C for 24 hours.

Thermal properties of the prepared PLA films obtained from DSC analysis are summarised in Table 4.5. In general, prepared films showed lower T_g , T_c , T_m and X_{DSC} values compared to raw PLA pellets. All of the prepared films showed lower T_g values compared to their respective PLA pellets. For instance, the T_g value for pure pellets was

determined to be 61.2°C while that of the prepared film immersed in water bath was reduced to 55°C. Reduction in T_g of prepared films could be due to the presence of solvent/moisture trapped inside the pores of the film. TGA analysis confirmed that the aforementioned film showed small amounts of weight loss. Another explanation could be that during the mixing step, the polymer dissolved in the solvent (DMSO) and subsequent polymer crystals starts to break down which consequently increases the polymer mobility. As a result of this, there is a decrease in thermal properties i.e. T_g and hence T_c . It is important to note that the reduction in T_g allows the crystallisation process to start at a lower temperature (Fehri *et al.*, 2016). This is particularly the case for pure pellets and prepared films immersed in water bath for which the T_c values are 128.4°C and 90.3°C, respectively. Furthermore, all of the films showed two melting peaks. The first peak corresponds to the melting of thinner crystals with lower thermal stability while the second peak corresponds to the melting of crystals with higher thermal stability (Fehri *et al.*, 2016, Di Lorenzo, 2006). Tee *et al.* (2013) stated that double peaks of melting usually happens in PLA with high L-lactide content. Many authors in previous literature have reported that the mechanism behind this behaviour is possibly due to the melt-crystallisation behaviour whereby PLA can crystallise into two crystalline phases i.e. α' and α (Tee *et al.*, 2013, Wasanasuk and Tashiro, 2011, Fehri *et al.*, 2016). The α' phase is due to the fusion of crystals with lower thermal stability whereas the α phase is due to crystals with higher thermal stability (Wasanasuk and Tashiro, 2011, Di Lorenzo, 2006).

Table 4.5: Thermal properties of PLA films prepared using a PLA concentration of 5wt% obtained from the first heating of TGA analysis. The thermal properties for raw PLA pellets obtained from the second heating are also shown.

Immersion bath	T _g (°C)	T _c (°C)	T _m (°C)	χ _{DSC} (%)
<u>Pure Pellets</u>	<u>61.2</u>	<u>128.4</u>	<u>156.1</u>	<u>2.7</u>
Water	55.0	90.3	149.4	14.1
Water/MeOH	60.3	96.8	153.6	6.8
<u>Dried Pellets</u>	<u>60.8</u>	<u>127.9</u>	<u>156.0</u>	<u>1.6</u>
Water	59.2	95.3	154.8	21.9
Water/MeOH	60.5	102.0	157.2	6.5
<u>Melted Pellets</u>	<u>61.0</u>	<u>130.5</u>	<u>156.3</u>	<u>1.5</u>
Water	60.6	99.9	158.3	1.6
Water/MeOH	61.0	102.6	156.0	7.8

Considering Table 4.5, no systematic results can be observed from the listed T_g values. Some films immersed in a water bath showed a higher T_g value whereas some films showed an increase in T_g when immersed in a water/MeOH bath. Comparing all prepared films at 5% PLA concentration, films immersed in water/MeOH had a higher T_g value compared to films immersed in the water bath. Furthermore, films prepared from dried and melted pellets showed improvements in terms of the glass transition temperature compared to films prepared from pure pellets. For example, the T_g value of the films immersed in 50/50% water/MeOH bath were recorded as 60.3°C, 60.5°C and 61.0°C, respectively.

PLA pellets and prepared films have almost a similar range of melting temperatures valued between 158.3 – 149.4°C. No remarkable improvements were noticed in T_m for films prepared from dried or melted pellets compared to films prepared from pure PLA pellets. According to the results obtained from DSC analysis, no changes in T_m were observed between films immersed in both water and 50/50% water/MeOH baths. This

suggests that the melting temperature is independent of the pellet treatment and the non-solvent use for the bath.

Considering Table 4.5, it can also be noted that all PLA pellets have a low degree of crystallinity due to its poor crystallisation ability (Zhang *et al.*, 2012). In contrast, most of the prepared films have higher crystallinity compared to their initial polymer pellets. This clearly indicates that the methodology for film preparation and respective parameters do have an effect on the crystallinity of the films. The increase observed in terms of the crystallinity of films is most likely associated with the rearrangement of polymer chains. This suggests that during film preparation, the PLA molecular chains were restructured to form crystalline ordered regions.

In comparing films prepared using a water immersion bath, films prepared from pure and dried pellets both showed higher crystallinity compared to films prepared with a water/MeOH immersion bath. The opposite can be observed for films prepared from melted pellets where the crystallinity of the films prepared with a water immersion bath had lower crystallinity compared to films prepared with a water/MeOH immersion bath.

Results obtained from the second heating of DSC analysis is shown in Table 4.6. The second heating indicates the thermal properties of PLA material as the thermal characteristics obtainable from the first heating is removed. From the results, it can be concluded that T_g and crystallinity both have clearly reduced compared to that of the first cycle while T_c values increased. Reduction in T_g is due to low mobility as a result of the film being heated in the first cycle. This led to the breaking of some of the chains and consequently lower crystallinity. Subsequently, this also led the films to retain their original material thermal characteristics.

Table 4.6: Thermal properties of PLA films prepared using 5wt% PLA concentration obtained from second heating. The result for raw PLA pellets obtained from second heating is also shown.

Immersion bath	T_g (°C)	T_c (°C)	T_m (°C)	χ_{DSC} (%)
<u>Pure Pellets</u>	<u>61.2</u>	<u>128.4</u>	<u>156.1</u>	<u>2.7</u>
Water	49.0	105.0	153.2	1.7
Water/MeOH	56.8	106.8	156.5	1.3
<u>Dried Pellets</u>	<u>60.8</u>	<u>127.9</u>	<u>156.0</u>	<u>1.6</u>
Water	56.2	109.7	156.2	1.3
Water/MeOH	59.2	116.5	156.8	1.3
<u>Melted Pellets</u>	<u>61.0</u>	<u>130.5</u>	<u>156.3</u>	<u>1.5</u>
Water	54.9	116.3	156.1	1.9
Water/MeOH	58.8	117.7	157.2	1.1

The thermal stability of films was studied via TGA and compared with results from their initial polymer pellets. These results are summarised in Table 4.7. In general, all fabricated films have lower thermal stability temperatures compared to their respective pellets. Considering the results, pure PLA pellets showed the highest thermal stability temperature at 329°C followed by the melted and dried pellets at 314°C and 318°C, respectively. All other fabricated films were found to decompose at lower temperatures. This clearly implies that the technique used for film preparation and/or conditions led to a reduction in decomposition temperatures.

Table 4.7: TGA results of PLA pellets and films prepared using 5wt% PLA concentration.

Immersion bath	Thermal stability at 5% (°C)	T_d (°C)	Residue at 600 °C (%)
<u>Pure pellets</u>	<u>329</u>	<u>361</u>	<u>1.10</u>
Water	304	350	1.24
Water/MeOH	285	339	0.96
<u>Dried pellets</u>	<u>314</u>	<u>343</u>	<u>0.78</u>
Water	303	347	0.99
Water/MeOH	293	340	0.26
<u>Melted pellets</u>	<u>318</u>	<u>346</u>	<u>1.19</u>
Water	299	346	0.89
Water/MeOH	289	339	0.81

It can be seen from Table 4.7 that films immersed in water bath have higher thermal stability compared to films immersed in 50/50% water/MeOH bath under the same preparatory conditions. This suggests that the reduction in film thermal stability might be highly affected by the nature of the non-solvent bath used during film formation. Films immersed in water bath showed lower thermal stability compared to their polymer pellet counterparts but exhibited higher thermal stability compared to when the films are immersed in water/MeOH bath. For instance, films prepared from pure PLA pellets at 5% concentration had a thermal stability of 304°C when immersed in a water bath but this reduced to 285°C in water/MeOH bath. Using water as a non-solvent bath causes degradation which consequently reduces overall thermal stability. However, the presence of MeOH in the non-solvent bath accelerated the degradation rate of films which rapidly shifted their thermal stability in the downward direction. For example, the film prepared at 5% PLA using a water bath showed a thermal stability of 304°C whereas the film immersed in water/MeOH bath showed a thermal stability of 285°C. This thus confirms that the presence of MeOH in the non-solvent affects the thermal

properties of films negatively. Results obtained from TGA analysis presented in Table 4.8 show that drying or melting PLA pellets prior to preparing the films does not improve its thermal stability.

Table 4.8: A comparison of weight loss of films prepared using 5% PLA concentration at 65°C, 100°C and 189°C.

Immersion bath	Weight Loss at 65 °C (%)	Weight Loss at 100 °C (%)	Weight Loss at 189 °C (%)
<u>Pure pellets</u>	<u>0.04</u>	<u>0.12</u>	<u>0.40</u>
Water	0.18	1.52	1.95
Water/MeOH	0.04	0.08	0.16
<u>Dried pellets</u>	<u>0.00</u>	<u>0.00</u>	<u>0.03</u>
Water	0.00	0.11	0.17
Water/MeOH	0.00	0.02	0.10
<u>Melted pellets</u>	<u>0.00</u>	<u>0.00</u>	<u>0.05</u>
Water	0.10	0.13	0.17
Water/MeOH	0.14	0.15	0.20

The weight loss of films at 65°C, 100°C and 189°C is shown in Table 4.8. Indications of the presence of MeOH and/or water and/or solvent (DMSO) trapped inside the pores at these temperatures can roughly be made. The temperatures were chosen according to the boiling points of MeOH, water and DMSO which have boiling points of 65°C, 100°C and 189°C respectively. Films which contain these components will evaporate resulting in a sharp reduction in weight loss as the boiling point is reached.

Most of the films did not show a significant reduction in weight loss at the boiling points of MeOH, water or DMSO. This indicates that implementing a normal oven as a drying technique is capable of removing most of a component's residue. For all of the prepared films, no MeOH residue was observed thus confirming that the aforementioned films do not contain any MeOH in their pores. This also indicates the quick evaporation of

MeOH which subsequently results in almost zero amounts of MeOH residue left inside pores of the film.

Some films showed a tiny amount of weight loss ranging between 0.02-0.15% at 100°C. It is most likely that these tiny amounts of weight loss indicate the adsorption of moisture from the ambient atmosphere by the films. Among all of the prepared films, film prepared from pure pellets at a 5% PLA concentration and immersed in water bath showed relatively larger amounts of weight loss compared to films prepared from dried and melted pellets. Similar observations were noticed at 189°C where the weight loss of this film sample was higher compared to other films. This indicates that the solvent and non-solvent did not fully mix due to their small pore sizes and that some amounts of solvent/non-solvent remained trapped inside the pores of the film. This incurs a difficulty for the solvent/non-solvent to escape easily from the pores. This has most likely occurred particularly for this sample but not as a consequence of the preparatory conditions.

The results for M_n , M_w and PDI of pure, dried and melted PLA pellets and their respective prepared films obtained from GPC analysis are summarised in Table 4.9. Pure PLA pellets showed the highest molecular weight with values of $M_n \approx 90.7\text{kDa}$ and $M_w \approx 162.6\text{kDa}$. Compared to pure pellets, both dried and melted pellets showed lower molecular weights. M_w will be considered and discussed in detail as it provides more representative data for the molecular weight distribution and size compared to M_n .

Table 4.9: Mn, Mw and PDI of PLA pellets and films prepared using 5wt% PLA concentration.

Immersion bath	M_n (kDa)	M_w (kDa)	PDI
<u>Pure Pellets</u>	<u>90.7</u>	<u>162.6</u>	<u>1.8</u>
Water	45.9	130.9	2.8
Water/MeOH	49.2	134.9	2.7
<u>Dried Pellets</u>	<u>81.8</u>	<u>149.8</u>	<u>1.8</u>
Water	46.5	127.8	2.7
Water/MeOH	47.4	117.2	2.5
<u>Melted Pellets</u>	<u>78.5</u>	<u>138.3</u>	<u>1.8</u>
Water	44.0	112.9	2.6
Water/MeOH	44.5	115.5	2.6

M_w values of PLA pellets and their respective films prepared in water and water/MeOH non solvent baths are shown in Figure 4.11. This gives the indication that the technique used in preparing the films and/or conditions led to a reduction in the molecular weight of the polymer. For example, the film prepared from pure pellets at 5% PLA concentration and immersed in water showed a M_w value of 130.9kDa, with a reduction of ≈20% compared to pure PLA pellets. Reduction in the value of M_w indicates that the polymer or film exhibits lower thermal stability. These results and observations are also in agreement with the results obtained from TGA analysis presented in Table 4.9. Reduction in M_w has most likely occurred due to the existence of water/moisture or other components that contributed to the degradation of PLA thus reducing its molecular weight. In terms of the procedures for film preparation, the films were immersed in a water or water/MeOH bath for a given period of time. It is during this step of film immersion that the PLA film starts to slowly degrade and as a result lowers M_w. Another possible and common reason is that the films may have adsorbed moisture from the atmosphere which increases the tendency for degradation to occur due to the presence of oxygen. In agreement, results obtained from TGA analysis confirmed that the

prepared films have lower thermal stability compared to their initial PLA pellets as shown in Table 4.7. Considering the step for mixing, films were prepared by dissolving polymer pellets at a temperature (80 °C) above the glass transition temperature of the polymer (≈ 60 °C) that may break up of some of the polymer chains thus leading to higher polymer mobility and reduction in the molecular weight of films. Results obtained from DSC analysis proved that prepared films have lower T_g values compared to their initial PLA pellets (Table 4.5).

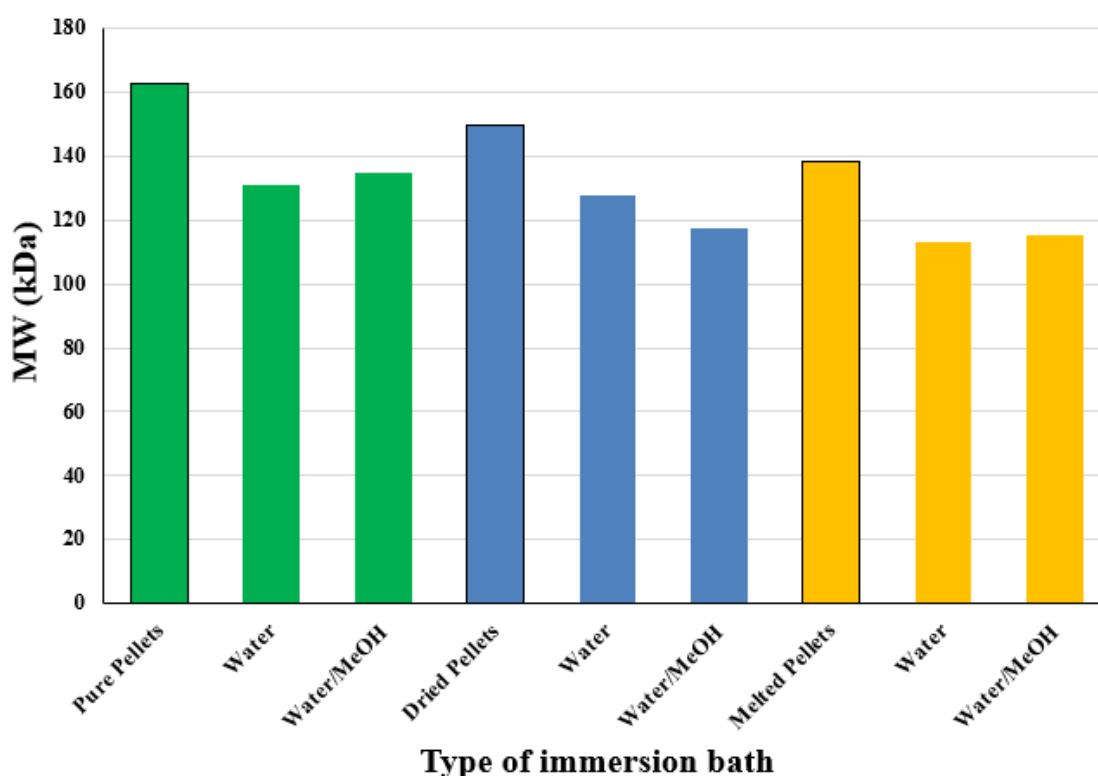


Figure 4.11: Average M_w of PLA pellets and their prepared films using 5% PLA concentration, and immersed in water and 50/50% water/MeOH bath.

Overall, no statistically significant changes were seen in the molecular weights between films immersed in a water bath or in 50/50% water/MeOH. Compared to films prepared at 5% PLA concentration with pure pellets, the M_w of films immersed in water and 50/50% water/MeOH were determined to be 130.9kDa and 134.9kDa, respectively. This implies that the type of non-solvent bath has no major effect on the molecular weight of films.

Chapter 4: Establishing Fabrication Conditions of Porous PLA Films

Generally, films prepared from dried or melted polymer pellets showed lower molecular weights compared to films prepared from pure pellets. Films prepared from pure pellets using a water bath has a M_w of 130.9kDa while films prepared from dried pellets has a reduced M_w of 127.8kDa. Further reduction in M_w was measured with a value of 112.9kDa for the film prepared from melted pellets using a water bath. The lower M_w of films prepared from dried and melted polymer pellets may indicate their low thermal stabilities. TGA analysis (Table 4.8) has proven that films prepared from dried and melted pellets have lower thermal stability and lower degradation temperatures compared to films prepared from pure pellets under the same preparatory conditions.

In summary of the above, SEM showed that films immersed in a water bath exhibited more continuous porous channels and better morphological microstructures compared to films prepared using 50/50% water/MeOH immersion bath. In addition, higher thermal stabilities were also determined for the films immersed in a water bath. According to the results obtained from DSC and GPC analysis, no differences in terms of thermal properties and molecular weights were found between films immersed in water and that of water/MeOH immersion bath (Table 4.6 and 4.9). In terms of cost, it is much cheaper to only use water for the non-solvent bath rather than using a mixture of water/MeOH.

In comparing films prepared from treated and untreated PLA pellets, less solid aggregation was observed via SEM imaging (Figure 4.8, 4.9 and 4.10) of films prepared from pure PLA pellets compared to films prepared from treated pellets. Relatively better thermal stability was also determined for films prepared from pure PLA pellets compared to the latter. No increase in thermal properties were observed for films prepared from treated pellets compared to pure pellets. Moreover, films prepared from treated pellets, more particularly those that were initially melted, have less surface

uniformity while also suffering from weakness/brittleness. According to the results obtained for thermal stabilities, images of film microstructure obtained from SEM imaging and surface morphology, it can therefore be concluded that films fabricated from pure PLA pellets using water as a non-solvent bath is associated with the most promising fabrication conditions to be considered for further investigations.

4.3.4 The effect of drying method

The effects of further drying the films after an initial drying at 40°C for 24 hours in a conventional oven were examined using a vacuum oven set at 25°C for 24 hours to remove any trapped solvents such as water, DMSO and methanol. Films dried in the vacuum oven showed shrinkages and were found to collapse after drying as shown in Figure 4.13. Three films were tested and confirmed similar observations. TGA analysis was used to determine whether drying by a conventional oven is adequate and capable of removing all the solvents or whether vacuum drying is essentially required for that same purpose. Results for weight loss obtained from TGA analysis shown in Table 4.10 showed nearly equal weight loss for films before and after drying thus clearly indicating that the usage of a vacuum oven for drying has no major effect in the removal of solvents. Therefore, a drying procedure of using a conventional oven set at 40°C for 24 hours was selected as it was able to produce films that do not exhibit any adverse effects on its structure.

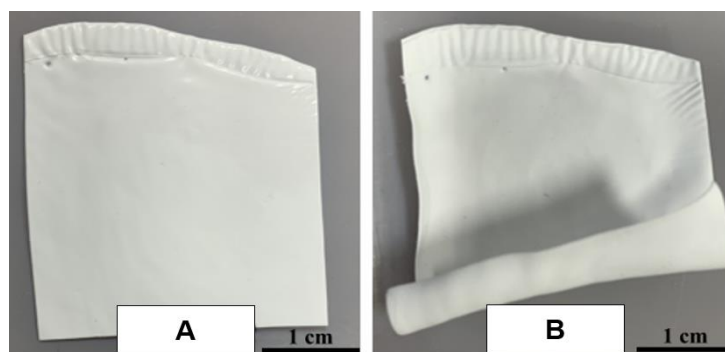


Figure 4.12: Structural changes of fabricated PLA film. (A) before and (B) after vacuum drying at 25 °C for 24 hours.

Table 4.10: A comparison of weight loss before and after vacuum drying at 65°C, 100°C and 189°C for selected films.

Film condition	Weight Loss at 65 °C (%)		Weight Loss at 100 °C (%)		Weight Loss at 189 °C (%)	
	No Vac.	Plus Vac.	No Vac.	Plus Vac.	No Vac.	Plus Vac.
Drying technique						
Pure pellets film	0.04	0.04	0.08	0.07	0.16	0.11
Dried pellets film	0.00	0.00	0.02	0.00	0.10	0.07
Melted pellets film	0.14	0.13	0.15	0.14	0.20	0.17

4.3.5 Determining the effects of PLA concentration

In determining the benefits of using raw pure PLA pellets and water as a non-solvent bath, the influence of PLA concentration on the morphology and properties of films was studied. Based on previous discussions, the most uniform films were determined to be fabricated with PLA concentrations of 5wt% and 10wt%.

The SEM images of PLA films prepared from pure pellets at 5% and 10% PLA concentrations with water as the non-solvent bath are shown in Figure 4.14. Both films show similar patterns of dense or low porous top layers with the formation of macro-void channels and finger-like structures in the cross-sections.

Comparison of surface images obtained from SEM (Figure 4.13- A2 and Figure 4.13 -B2) reveals that the formation of macro-voids on the surface increased as the PLA concentration decreased. This may be due to the effects of precipitation velocity. Domingues *et al.* (2016) observed that faster precipitation occurs at lower polymer concentrations which resulted in larger pores in the structure. Similarly, Mulder (1991) reported that by increasing polymer concentration, a higher concentration of

polymer in the film interface throughout its cross-sectional thickness can be obtained. This increases the polymer volume fraction which subsequently leads to lower porosity, a less porous top layer and therefore lower flux across the membrane. It is also important to mention here that generally lower fluxes may translate to higher solute rejection which is highly desirable for separation purposes.

Films prepared at 5% PLA concentration showed fewer solid aggregates of polymer compared to films prepared at 10% PLA concentration (Figure 4.13- A1 and Figure 4.13 -B1). This most likely occurs as a consequence of slow precipitation despite the polymer aggregation in 10% PLA film is considerably small and negligible. In terms of layer thicknesses SEM images showed that the films prepared at both concentrations exhibited almost similar measurements on the top and bottom layers. This was determined to be 20 μ m and 550 μ m, respectively.

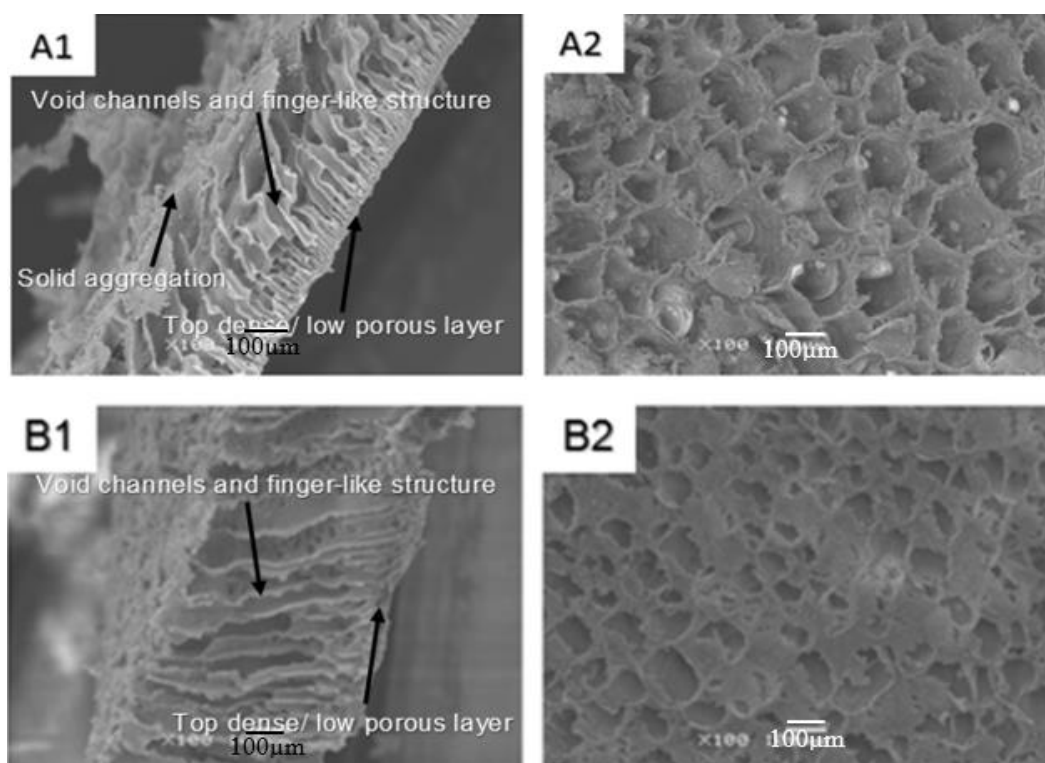


Figure 4.13: Cross-sectional and top view SEM images of films prepared from pure PLA with water immersion bath at PLA weight concentrations of (A1) & (A2) 10% and (B1) & (B2) 5%.

The thermal properties of PLA films prepared at 5% and 10% PLA concentrations obtained from DSC analysis is shown in Table 4.11. Results indicate that films prepared at 10% PLA concentration showed higher thermal properties compared to films prepared using 5% PLA concentration. This implies that films prepared with 10% PLA concentration exhibits lower polymer chain mobility which subsequently leads to the higher thermal stability. In addition, results obtained from TGA analysis proved the presence of water and solvent residues in films prepared with 5% PLA concentration which perhaps contributed to the reduction in its respective thermal properties. Considering crystallinity, DSC analysis results shows that preparing films at 10% PLA concentration has improved the crystallinity by 5.6% from 14.1% exhibited by films prepared at 5% PLA concentration.

Table 4.11: Thermal properties of films prepared from pure PLA using a water immersion bath at 5% and 10% PLA concentrations obtained from first heating of DSC.

Film condition	T_g (°C)	T_c (°C)	T_m (°C)	χ_{DSC} (%)
10% con.	60.1	94.6	154.9	19.7
5% con.	55.0	90.3	149.4	14.1

Film stabilities were investigated via TGA and a comparison for films prepared at 5% and 10% PLA concentrations were made. These results are summarised in Table 4.12. Films prepared at a concentration of 10% PLA showed relatively higher thermal stability compared to films prepared at 5% PLA. The thermal stability of a PLA concentration of 10% was found to be 311°C while the thermal stability at 5% PLA concentration is 304°C. In addition, results indicated that the preparation of films with 10% PLA concentration improved the temperature for degradation by only 1°C. This subsequently implies that making alterations in terms of polymer concentration does not play a big role on thermal stability.

Table 4.12: Results obtained from TGA analysis for films prepared from pure PLA at PLA concentrations of 5% and 10% with a water immersion bath.

Film condition	Thermal stability at 5%	T_d	Residue at 600 °C
	(°C)	(°C)	(%)
10% con.	311	351	0.71
5% con.	304	350	1.24

The weight loss of films at 100°C and 189°C corresponding respectively to the boiling points of water and DMSO are shown in Table 4.13. At 100°C, films prepared at 5% PLA concentration indicated a weight loss of only 1.52% which is possibly due to the adsorption of moisture from the ambient atmosphere. PLA is not entirely hydrophobic which thus permits water adsorption to occur to some extent. Hendrick and Frey (2014) has reported that PLA has the ability to absorb some water. At 189°C, the weight loss of the same sample was also small measuring at only 1.95%. This may indicate that some amount of solvent is trapped inside the pores of the films which are difficult to easily escape from the pores during drying. At 10% concentration the PLA films prepared showed very tiny amounts of weight loss at 100°C and 189°C which was determined to be 0.26% and 0.41% respectively.

Table 4.13: A comparison of weight loss at 100°C and 189°C for films prepared from pure PLA with PLA concentrations of 5% and 10% using a water immersion bath.

Film condition	Weight Loss at 100 °C	Weight Loss at 189 °C
	(%)	(%)
10% con.	0.26	0.41
5% con.	1.52	1.95

Films prepared using a PLA concentration of 10% showed lower molecular weights compared to films prepared using 5% PLA as shown in Table 4.14. The low molecular weight for the film prepared using 10% PLA concentration cannot be implied to be due

to its low thermal stability since results obtained from TGA and DSC analysis clearly proved otherwise. A possible explanation could be that the polymer chains in the film prepared using 5% PLA concentration is longer and more continuous compared to that of the films prepared using 10% PLA concentration film. This long and continuous polymer chain is achievable through casting. Despite the small difference in molecular weights between films prepared using 5% and 10% PLA concentration, the PDI was only measured to be 0.2.

Table 4.14: M_n , M_w and PDI of films prepared from pure PLA with PLA concentrations of 5% and 10% using a water immersion bath.

Films concentration	M_n (KDa)	M_w (KDa)	PDI
10%	43.5	111.3	2.6
5%	45.9	130.9	2.8

By drawing a general comparison between films prepared using PLA concentrations of 5wt% and 10wt%, it can be concluded that both films showed relatively similar patterns in terms of their morphological structure and properties. With further detailed evaluations of the latter type of film, continuous porous channels were found more along the width of the film with less aggregation. In addition, the thermal properties i.e. T_g and crystallinity was determined to be higher for films prepared using 10wt% PLA concentration. In tandem to the above, TGA analysis also showed higher thermal stability in addition to less weight loss. Through the above discussions, films fabricated using 10wt% PLA concentration was given the main priority to be considered and selected. With this, the preparatory conditions and parameters were further established to fabricate flat porous PLA films.

4.3.6 The influence of thickness on film properties

In Sections 4.2.2.1-4.2.2.5, the most conducive preparatory conditions and parameters that contribute towards controlling and influencing the morphology and properties of fabricated films were explored. The thickness for all fabricated films during initial casting was fixed to be 150 μm . From there, the optimum fabrication conditions to produce flat porous film sheets were selected. Despite this, fabricated films were found to suffer from shrinkage and tension on the surface of the films. Film shrinkages lead to the formation of non-continuous and non-uniform flat film sheets. This possibly leads to non-uniform microstructural morphology, and hence most likely non-uniform pore size and ultimately unstable flux as a consequence.

To overcome this, controlling and improving the surface morphology of the film is thus required. In this section, the influence of film thickness will be explored from which the optimum morphological surface structure able to be achieved will be determined.

Surface structure morphologies of PLA films fabricated with initial thicknesses of 150 μm , 100 μm , 50 μm and 25 μm are shown in Figure 4.14. All the films were prepared using a PLA concentration of 10% PLA and casted on a glass substrate before being immersed in a non-solvent water bath at 25°C for 24 hours. Results showed significant improvements in terms of film morphology as the thickness was decreased. Shrinkages were not observed at films fabricated with initial thicknesses of both 50 μm and 25 μm . In addition, flat and continuous top and bottom uniform surfaces were also formed for the aforementioned films. Brittleness, most likely due to its thickness was however observed for the film casted at 25 μm . Shrinkage and surface tension was observed for films prepared with initial thicknesses of 150 μm and 100 μm .

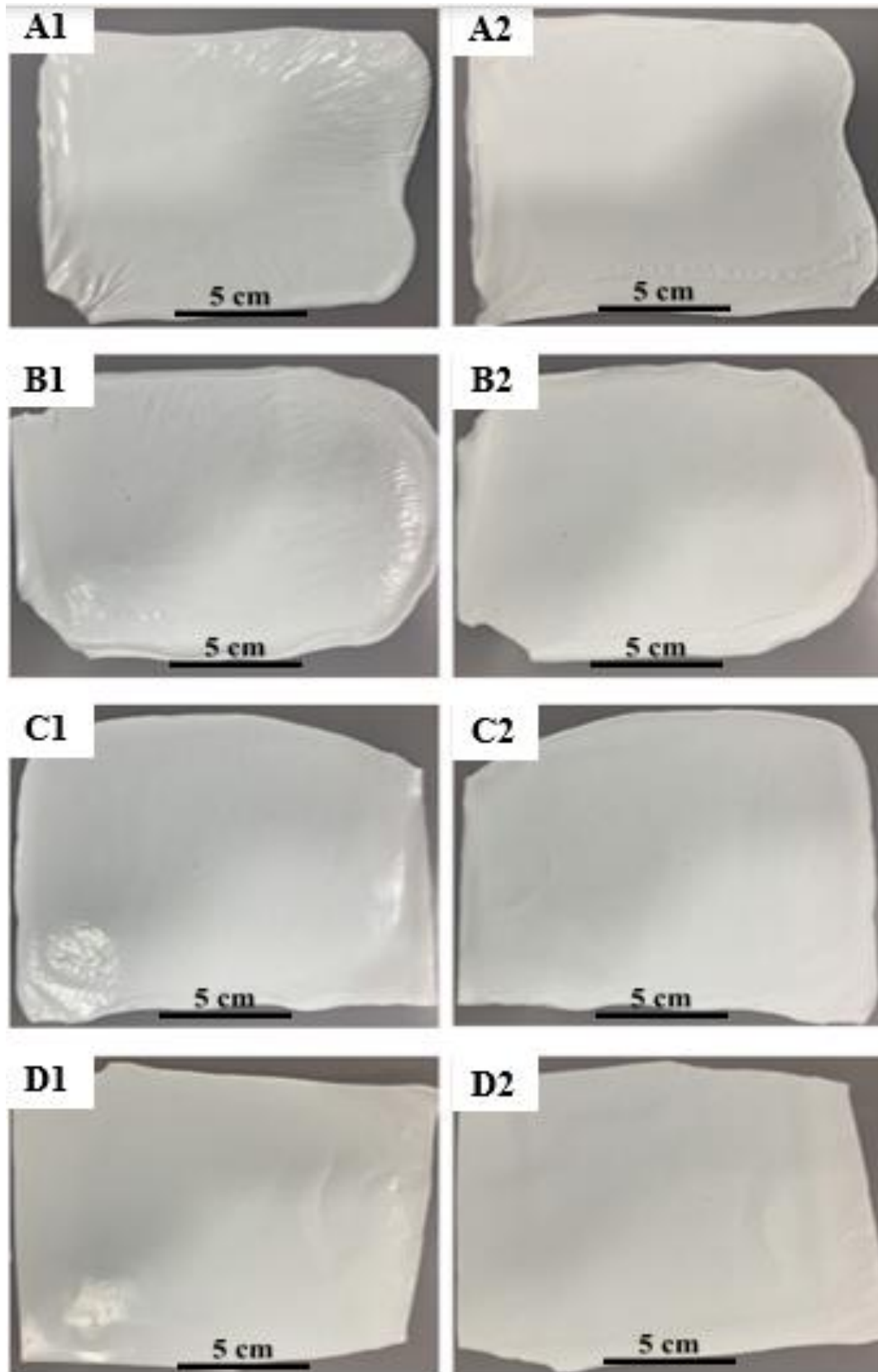


Figure 4.14: Top and bottom sides of the PLA films casted at different initial thicknesses. (A1) top view side of 150 μm film, (A2) bottom view side of 150 μm film, (B1) top view side of 100 μm film, (B2) bottom view side of 100 μm film, (C1) top view side of 50 μm film, (C2) bottom view side of 50 μm film, (D1) top view side of 25 μm film and (D2) bottom view side of 25 μm film. All the films were casted on glass substrates.

SEM images of PLA films prepared from pure pellets casted with initial thicknesses of 150 μ m, 100 μ m, 50 μ m and 25 μ m using a PLA concentration of 10% and immersed in water bath are shown in Figure 4.15. The films were found to exhibit a pattern of dense or low porous top layers with the formation of macro-void channels and finger-like structures in the cross-sections. This is most likely due to the quick formation of the top layer. In addition, the SEM images also showed non-uniform pore sizes and structure. The thickness of the top layer was determined to be around 20 μ m for all the films regardless of their initial casting thickness. The thickness of the bottom layer however varies. More particularly, films casted with initial thicknesses of 150 μ m, 100 μ m, 50 μ m and 25 μ m exhibited bottom region thicknesses of approximately 650 μ m, 550 μ m, 260 μ m and 160 μ m respectively. With the above, it is implied that changing the thickness of the initial casting only effects the thickness of the bottom region and not the top layer.

As seen from Figure 4.15, the finger-like structures and pores channels form correspondingly with the increase in initial film thickness. Increase in the amount of solid aggregation of PLA polymers was also found to be formed on the bottom region of the films with increasing film thickness. The formation of the morphological structures of the films are due to the different precipitation mechanisms that take place on the top and bottom regions. As discussed previously, the early formation of the top region reduces the diffusion of solvent and non-solvent which subsequently leaves the bottom region as a polymer-rich phase. This is clearly indicated for the films fabricated with initial thicknesses of 150 μ m and 100 μ m, and partially for films fabricated with initial thicknesses of 50 μ m and 25 μ m.

Cross-sectional images of films fabricated with an initial thickness of 150 μ m and 100 μ m (Figure 4.15-A1 and Figure 4.15-B1) show finger-like structures in the top

region with solid aggregates of polymer on the bottom region. The film with a 50 μ m initial casting thickness (Figure 4.15-C1) was observed to exhibit pore channels with finger-like structures along the film's cross section with the formation of a small layer of solid PLA aggregation. Considering the film fabricated with a 25 μ m initial casting thickness, sponge-like structure with some folded layers can be observed (Figure 4.15-D1).

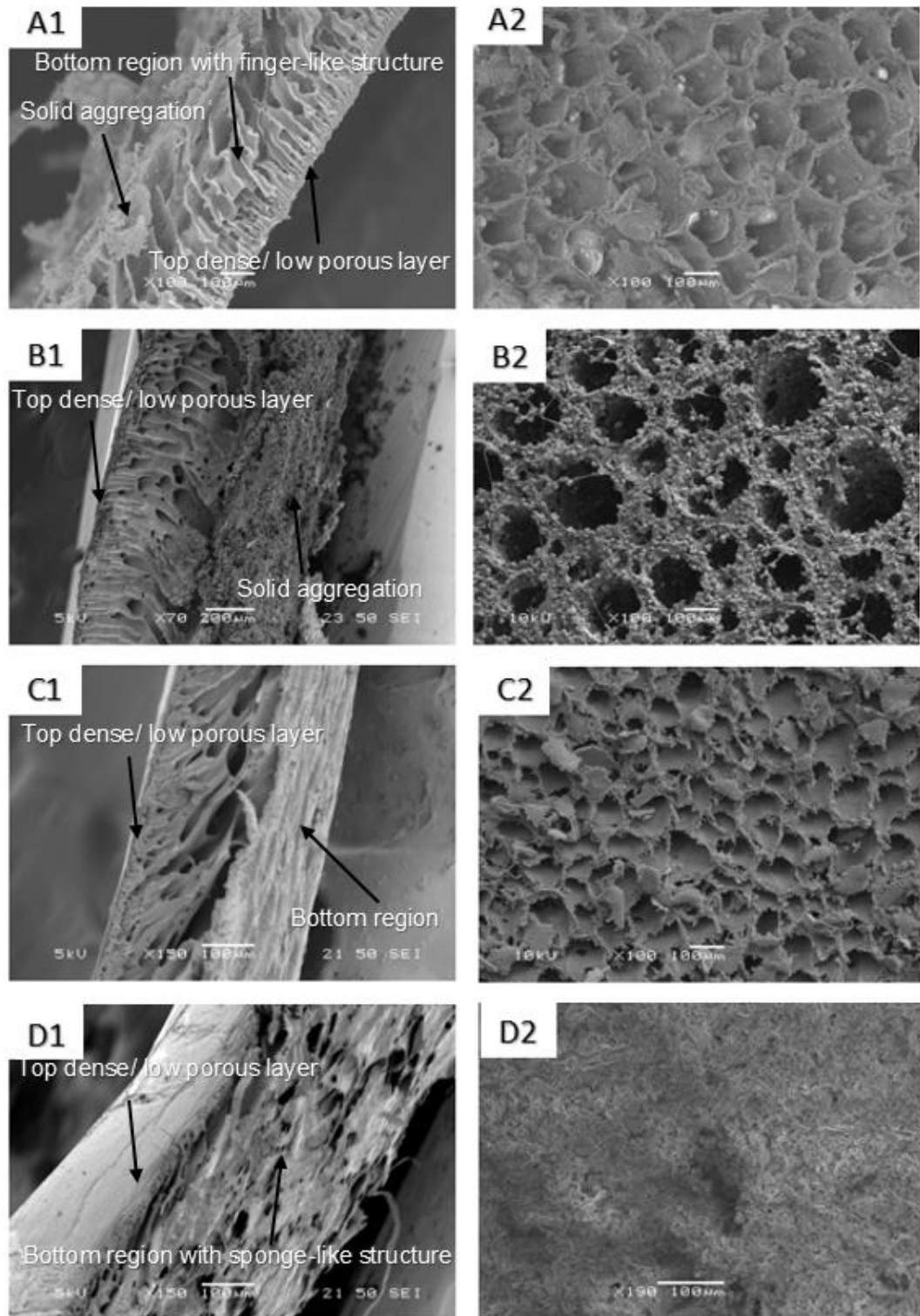


Figure 4.15: SEM images showing the top and cross-sectional views of films with initial film thicknesses of (A1) top view side of 150 μm , (A2) cross-sectional view side of 150 μm , (B1) top view side of 100 μm , (B2) cross-sectional view side of 100 μm , (C1) top view side of 50 μm , (C2) cross-sectional view side of 50 μm , (D1) top view side of 25 μm and (D2) cross-sectional view side of 25 μm . All the films were prepared using pure PLA with 10% PLA concentration and immersed in water bath.

Considering all the prepared films, results of XRD analysis shown in Figure 4.16 confirms the presence of PLA polymers and that they have not been destroyed or have lost its crystalline structure due to phase inversion. XRD demonstrated the crystallinity of PLA in terms of crystals peaks at 16.9° , 19.1° and 22.6° which is characteristic of the XRD analysis for PLA polymer.

From Figure 4.16 it can be clearly observed that films fabricated at higher initial thickness exhibit higher crystallinity. The crystallinity has a direct proportional relationship with the casting thickness where the crystallinity increases with increasing casting thickness and vice versa. In agreement with the results obtained from XRD analysis, results from DSC confirmed that films fabricated with lower casting thicknesses has lower crystallinity compared to films with thicker thicknesses. According to Figure 4.16, films fabricated at $150\mu\text{m}$ and $100\mu\text{m}$ mainly showed sharp clear PLA peaks characteristic of semi-crystalline structures. The film fabricated at $150\mu\text{m}$ has one large peak at 16.9° and two smaller ones at 19.1° and 22.6° . Only one large peak at 16.9° and a small one at 19.1° was observed for the film fabricated at $100\mu\text{m}$. On the other hand, films fabricated at initial casting thicknesses of $50\mu\text{m}$ and $25\mu\text{m}$ exhibited almost an amorphous-like structure rather than a semi-crystalline structure since sharp PLA peaks were not observable. The film with $50\mu\text{m}$ initial casting thickness exhibited a pure amorphous-like structure, whereas a semi amorphous-like crystal structure, probably destroyed crystal structure, was observed for the $25\mu\text{m}$ film thickness. This thus concludes that the parameter for casting thickness has a significant effect on the film's crystalline structure.

Variance in the crystal structure and crystallinity of PLA films is probably mainly associated with the casting step since this is the only step that has changed in this investigation while all other parameters and preparation conditions have been fixed.

Casting has been found to have an effect on film formation, and solvent and non-solvent phase exchange which caused changes in terms of the crystal structures of films. It is most likely that with the films forming quickly at low casting thicknesses, time was not enough for the polymer molecular chains to restructure themselves to be ordered in a regular manner. The opposite phenomena perhaps happened where at thicker thicknesses the PLA chains had enough time to rearrange and be ordered in a regular manner which thus led to higher crystallinity. In agreement with the above discussion, it was clearly evident that films with a thin thickness formed much quicker than the ones with thicker thicknesses.

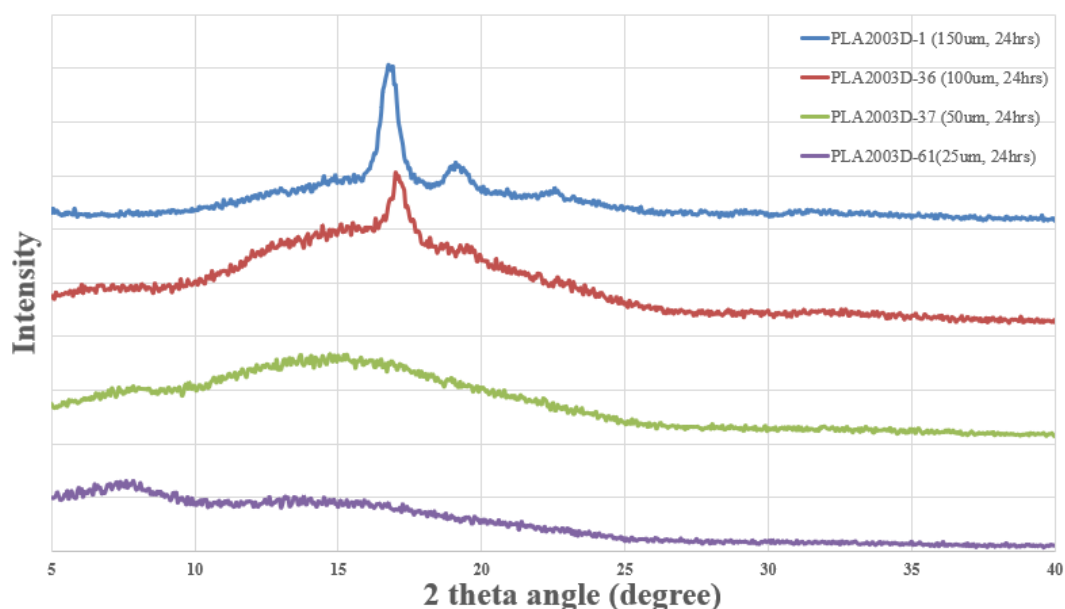


Figure 4.16: XRD data for film crystals from 5° to 40°. The films were prepared from pure PLA with 10% PLA concentration at initial casting thicknesses of 150µm, 100µm, 50µm and 25µm and immersed in water bath.

Thermal properties of the films prepared from pure PLA with a concentration of 10% PLA and immersed in water bath at initial casting thicknesses of 150µm, 100µm, 50µm and 25µm analysed by DSC are summarised in Table 4.15. The results showed that the preparation of films at the different casting thicknesses, have no overall effect on thermal properties i.e., T_g , T_c and T_m . Significant influence of changing the thickness of the casting was however observed in terms of the film's crystallinity. Considering Table

4.15, the thicker films i.e. 150 μ m and 100 μ m was found to exhibit doubled the percentage crystallinity when compared to thinner films i.e. 50 μ m and 25 μ m. This observation is in agreement with the results obtained from XRD analysis which has already been presented earlier and explained. In addition, Mulder (1991) stated that low crystalline content in the resulting membrane can be observed for most semi-crystalline polymers due to quick membrane formation. In conclusion, casting thickness has no effect on the thermal properties of films but however influences the crystallinity where the percentage crystallinity correspondingly increases with increasing film thickness.

Table 4.15: Thermal properties of films prepared from pure PLA with 10% PLA concentration and immersed in water bath at initial casting thickness of 150 μ m, 100 μ m, 50 μ m and 25 μ m obtained from first heating of DSC.

Film thickness	T _g (°C)	T _c (°C)	T _m (°C)	χ_{DSC} (%)
150μm	60.1	94.6	154.9	19.7
100μm	59.5	97.3	156.3	17.7
50μm	59.7	95.3	155.8	8.1
25μm	60.0	93.3	154.5	7.6

The stability of films prepared from pure PLA with 10% PLA concentration and immersed in water bath at casting thicknesses of 150 μ m, 100 μ m, 50 μ m and 25 μ m were studied via TGA. The results obtained are summarised in Table 4.16. Films fabricated at 100 μ m and 50 μ m showed the highest thermal stability and degradation temperatures compared to films fabricated at 150 μ m and 25 μ m. More particularly, films casted with a thickness of 100 μ m and 50 μ m have a T_d of 362°C and 361°C, respectively whereas T_d reduced to 351°C for both films casted at 150 μ m and 25 μ m. Furthermore, results obtained from TGA reveal that films fabricated at 100 μ m and 50 μ m have the lowest residue at 600°C compared to other films thus giving them the priority to be selected along with their relatively high thermal stability.

Table 4.16: Results obtained from TGA analysis of films prepared from pure PLA2003D with 10% PLA concentration and immersed in water bath at initial casting thicknesses of 150µm, 100µm, 50µm and 25µm.

Film thickness	Thermal stability at 5%	T_d	Residue at 600 °C
	(°C)	(°C)	(%)
150µm	311	351	0.71
100µm	320	362	0.40
50µm	314	361	0.42
25µm	293	351	4.40

The weight loss of films at the boiling points of water and DMSO i.e. 100°C and 189°C respectively are presented in Table 4.17. At both temperatures, no remarkable weight loss was observed for all the fabricated films with varying thicknesses. These tiny amount of losses ranging between 0.26-0.54% is most likely associated with the moisture adsorbed by the surrounding atmosphere and/or errors in the measuring instrument. This therefore suggests that fabricating films at varying casting thicknesses do not cause the film to adsorb or trap DMSO solvent or water. It shall be noted here that the drying of films using a conventional oven set at 40°C for 24 hours as the drying method was capable and successful in evaporating any liquid residues at all film thicknesses.

Table 4.17: Weight loss at 100°C and 189°C for films prepared from pure PLA with 10% PLA concentration and immersed in water bath at initial casting thicknesses of 150µm, 100µm, 50µm and 25µm.

Film thickness	Weight Loss at 100 °C	Weight Loss at 189 °C
	(%)	(%)
150µm	0.26	0.41
100µm	0.53	0.54
50µm	0.35	0.36
25µm	0.32	0.33

4.3.7 Physical properties

Actual thicknesses of PLA films fabricated at initial casting thicknesses of 150 μ m, 100 μ m, 50 μ m and 25 μ m are tabulated in Table 4.18 and graphically presented in Figure 4.17. For all the films, a significant growth of 400-600% in thickness was measured in comparison to their initial casting thickness. It is expected that the growth in film thickness occurred during phase inversion as the films are immersed in a non-solvent bath. The thicknesses of the films were measured at two different stages; the ‘wet base’ i.e. immediately after film formation, and ‘dry base’ i.e. after the drying step. Results in Table 4.18 show that films have approximately similar range of thickness values measured at ‘wet base’ and ‘dry base’ stages which confirms that the growth in thickness is caused by phase exchange and not as a result of drying.

Table 4.18: A comparison of thickness measurements before and after drying step.

Film's condition	Wet base (μm)	Dry base (μm)
150μm	809 $\pm$ 65	801 $\pm$ 68
100μm	671 $\pm$ 52	677 $\pm$ 49
50μm	290 $\pm$ 28	293 $\pm$ 30
25μm	123 $\pm$ 11	121 $\pm$ 10

Note: Thickness measurements obtained immediately after film formation. i.e. ‘wet base’, and after the drying step i.e. ‘dry base’ for films prepared from pure PLA with 10% PLA concentration and immersed in water bath at initial casting thicknesses of 150 μ m, 100 μ m, 50 μ m and 25 μ m.

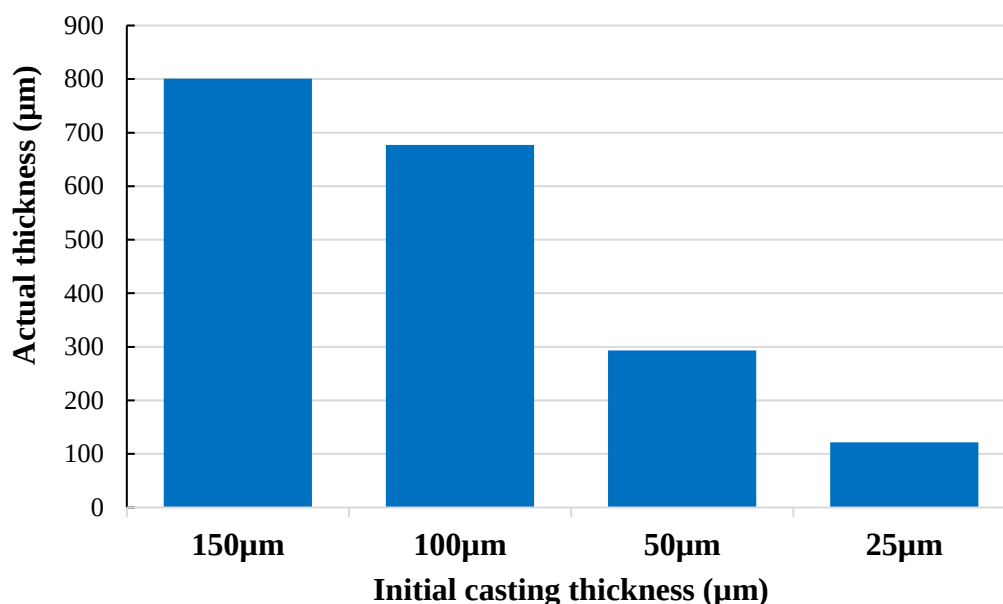


Figure 4.17: Actual thickness measurements the films prepared from pure PLA with 10% PLA concentration and immersed in water bath at initial casting thicknesses of 150μm, 100μm, 50μm and 25μm.

The growth in the thickness of the films is associated and explained by “swelling” (Cliff, 2011). The volume of PLA films expand during the formation of films where phase exchange occurs between solvent and non-solvent. As a consequence, swollen films with pores were formed to characterise the film with a high porosity. The mass of the films fabricated with initial casting thicknesses of 150μm, 100μm, 50μm and 25μm are shown in Figure 4.18. The mass of the films were found to increase with increasing thickness. This is due to the amount of PLA polymers in thicker films which is approximately 2-4 times more than the ones in thinner films. In other words, the mass per unit area of the film has a direct relationship with film thickness where the mass per unit area increases with increasing film thickness.

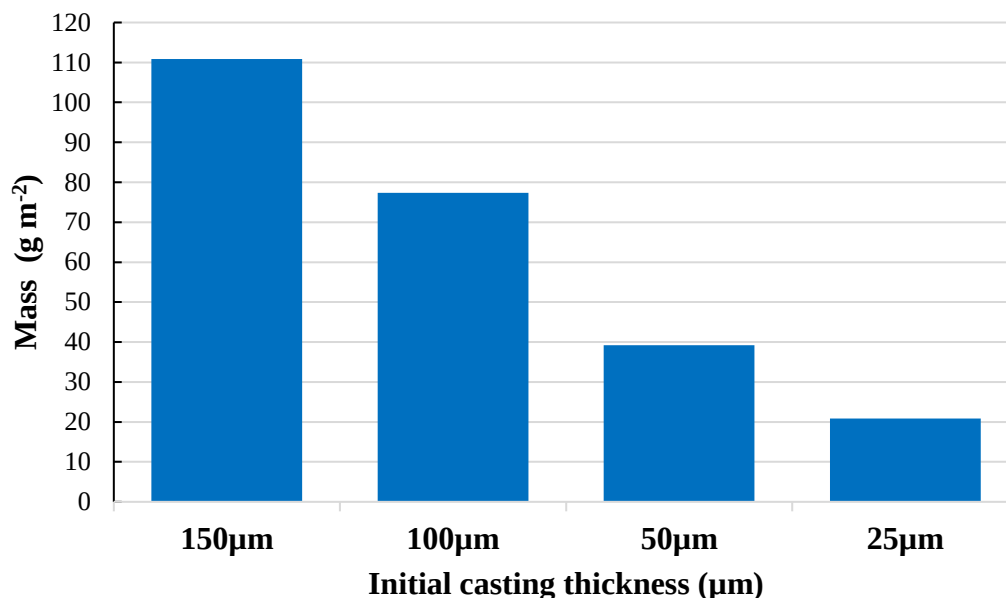


Figure 4.18: Mass measurements of films prepared from pure PLA with 10% PLA concentration and immersed in water bath at initial casting thicknesses of 150μm, 100μm, 50μm and 25μm.

The density and porosity measurements of PLA films at initial casting thicknesses of 150μm, 100μm, 50μm and 25μm are shown in Figure 4.19. Density and porosity have an inverse relationship whereby an increase in casting thickness decreases the density and consequently increases the porosity. This applies for all fabricated films except for the film casted with an initial thickness of 150μm.

In general, higher porosity indicates that the film exhibits more voids in the form of pores which is filled with air. The density of PLA is approximately 1.24g cm^{-3} while the density of air is approximately 0.001g cm^{-3} . By considering the aforementioned densities along with the total volume of the film, the volume of the voids occupied with air, which has negligible density, led to a reduction in total film density. With this, density decreases and hence porosity increases with increasing casting thickness since the formation of films with thicker initial casting thickness is relatively slower than thinner ones. The trend of exhibiting an increase in porosity with increase in casting thickness was observed for the all films except for the film fabricated with an initial casting thickness of 150μm. Despite that the film fabricated with an initial casting of

150 μm did not follow a similar trend, it can be observed that the density is comparably high as a result of low porosity. Considering the films, the density were determined to be 0.172g cm⁻³, 0.134g cm⁻³, 0.114g cm⁻³ and 0.138g cm⁻³ for the films casted with initial thicknesses of 25 μm , 50 μm , 100 μm and 150 μm respectively. In addition, a 86.1%, 89.2%, 90.8% and 88.8% porosity were measured for the same films, respectively.

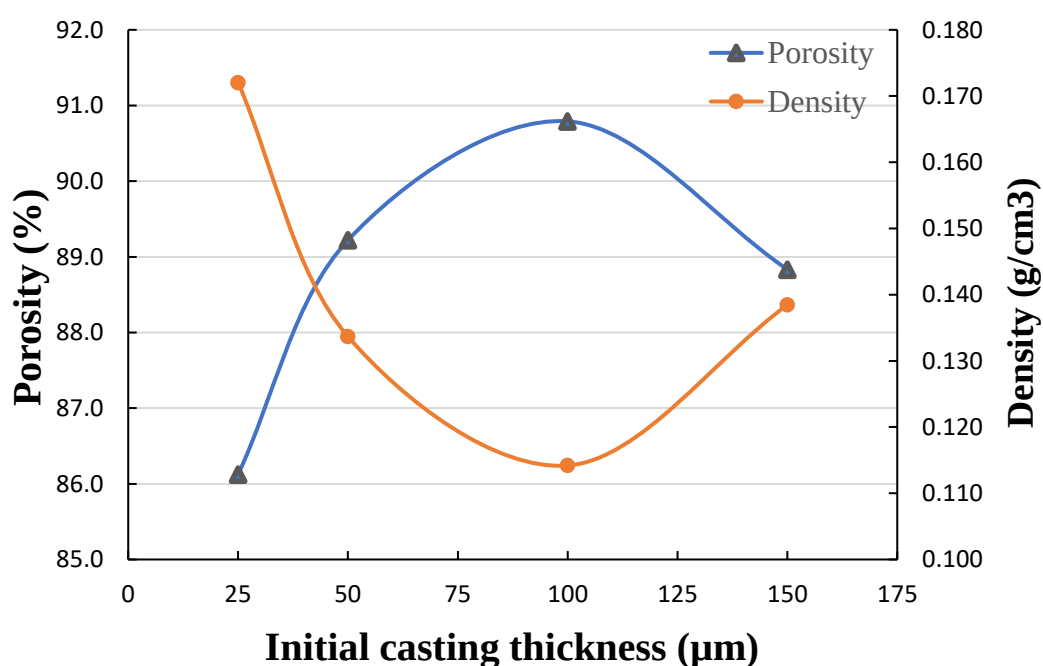


Figure 4.19: Density and porosity measurements of films prepared from pure PLA with 10% PLA concentration and immersed in water bath at initial casting thicknesses of 150 μm , 100 μm , 50 μm and 25 μm .

4.3.8 Fabrication of porous PLA films using alternative PLA grades

LR708 S is a high purity PLA grade that is mainly used for medical applications. With an amorphous structure, it has a high molecular weight i.e. approximately 1500kDa. In furthering the study, this amorphous PLA grade will be explored for fabrication of porous PLA films and will be discussed in this section. The purpose of this investigation is to understand to what extent the established fabrication technique of porous PLA films

can be applied for different PLA grades, and perhaps to alternative biopolymer in the future.

The XRD of PLA LR708 S polymer film is shown in Figure 4.20. The result shows that the aforementioned PLA grade has one wide amorphous peak, with no sharp peak in its crystal structure thus confirming that the LR708 S exhibits an amorphous-like structure.

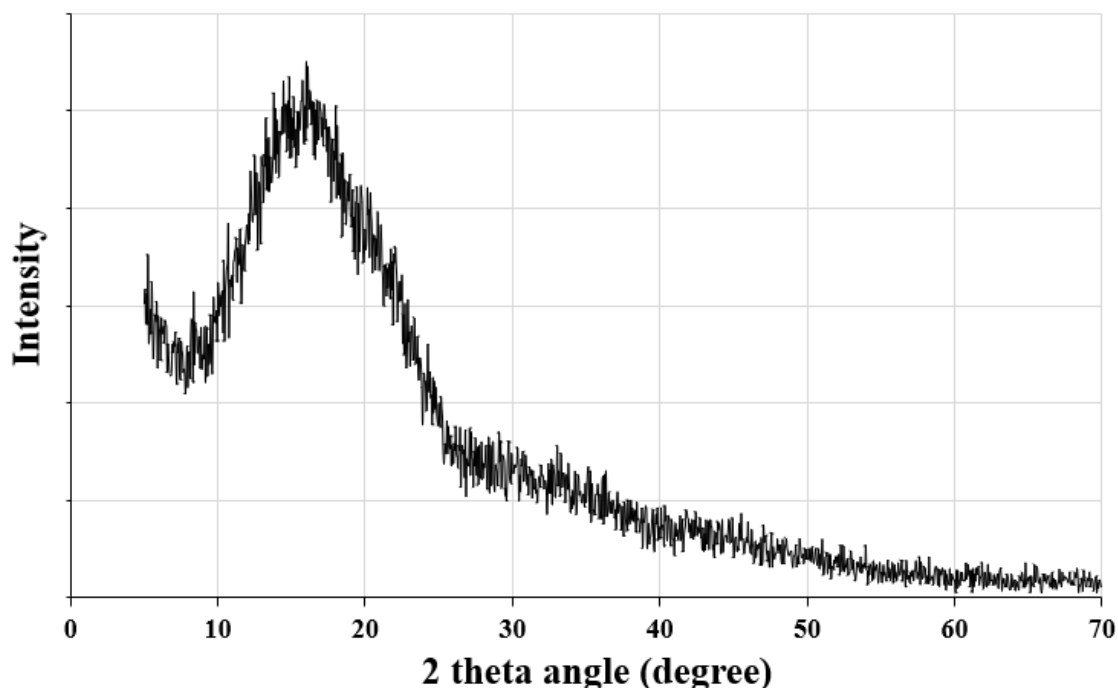


Figure 4.20: XRD data for PLA LR708 S crystals from 5° to 70°. The film was prepared from LR708 S with 5% PLA concentration using DMSO solvent and immersed in a water non-solvent bath. Both mixing (at ≈ 80 °C) and immersion in non-solvent bath (25 °C) were for 24 hours. Casted at 150 μm . Resulted films were dried in the oven at (40 °C) for 24 hours.

SEM images of LR708 S films prepared with 5/95wt%, 7.5/92.5wt% and 10/90wt% polymer/solvent ratios are shown in Figure 4.21. A uniform continuous film was only observed with films prepared with the 5/95 ratio whereas those prepared with 7.5/92.5 and 10/90 ratios were not continuous and irregular. The latter films also suffered from surface tension and stresses during the solvent exchange process with the presence of stretch marks and teared sections. According to SEM images of the top view, prepared films exhibited some pores on the surface. However by observing cross-sectional SEM

images, it can be deduced that the films prepared with 7.5/92.5 and 10/90 ratios exhibit pore formations that have either not initiated or completed.

Mulder (1991) has reported that with increasing polymer concentration, a higher polymer concentration in the film interface can be obtained thus leading to an increase in polymer volume fraction. The low porosity along with a less porous top layer leads to a lower flux across the membrane. This phenomena can also be explained through the effects of precipitation velocity. According to previous literature (Domingues *et al.*, 2016), faster precipitation was observed at lower polymer concentrations which resulted in larger pores in the structure.

During film preparation, the polymer mixture became more viscous as the polymer/solvent ratio was increased thus making film casting difficult. Noting that the molecular weight of LR708 S PLA grade is high ($\approx 1500\text{kDa}$), even a small increase in polymer concentration can change the viscosity of the mixtures. Similar effects between concentration and viscosity was studied by Zhou *et al.* (2010) for polyethersulfone. They concluded that the viscosity of the solution increased with increasing polymer molecular weight and polymer concentration. In summary, based on the morphological surface structure and microstructure a PLA LR708 S film with 5wt% polymer concentration was successfully fabricated from amorphous raw PLA pellets.

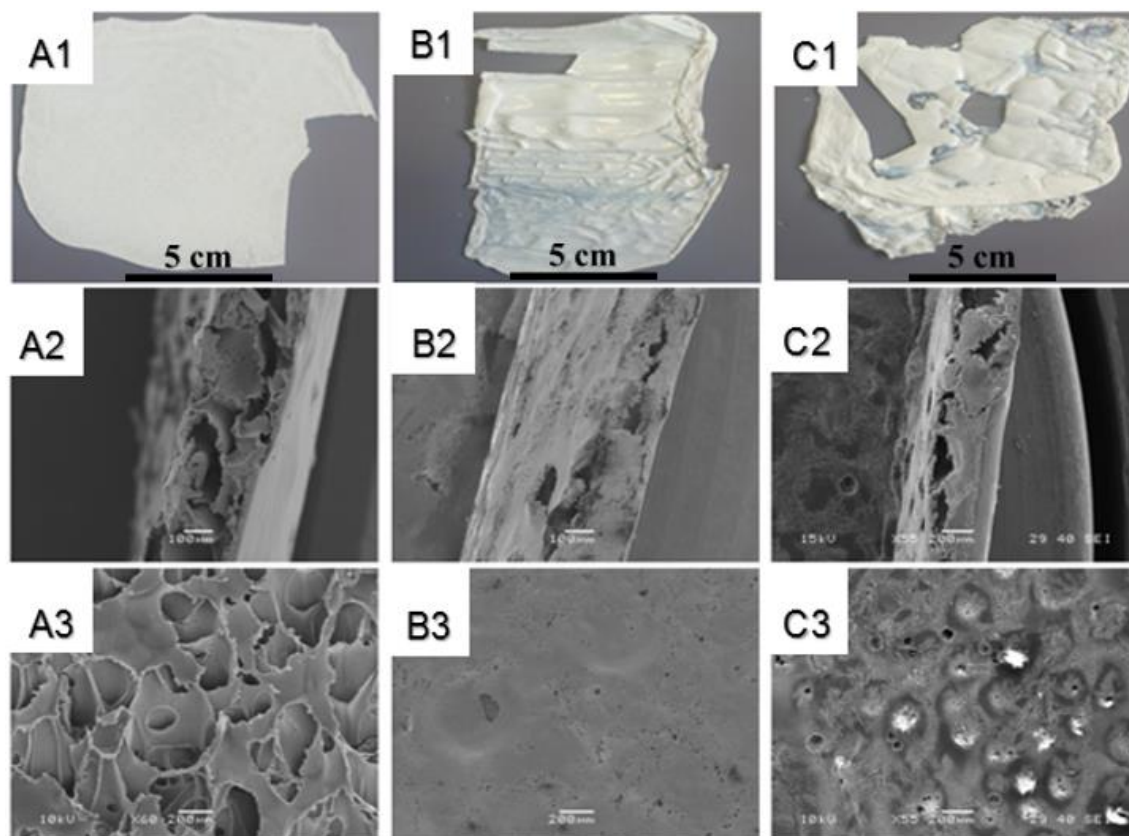


Figure 4.21: SEM images and surface morphologies of LR708 S films prepared using PLA/DMSO wt/wt % concentrations of (A1) optical surface morphology, (A2) cross-sectional SEM image and (A3) porous side SEM image 5/95, (B1) optical surface morphology, (B2) cross-sectional SEM image and (B3) porous side SEM image 7.5/92.5 and (C1) optical surface morphology, (C2) cross-sectional SEM image and (C3) porous side SEM image 10/90 and immersed in a non-solvent water bath. The films were casted with a thickness of 150 μ m. Non-solvent bath=water. Both polymer/solvent mixing (at ≈ 80 $^{\circ}$ C) and immersion in non-solvent bath (25 $^{\circ}$ C) were for 24 hours. Casted at 150 μ m. Resulted films were dried in the oven at (40 $^{\circ}$ C) for 24 hours.

4.4 Summary

In this chapter, flat PLA film sheets were prepared with various preparatory conditions via the phase inversion – immersion precipitation technique. The effects of pre-treating the PLA pellets prior to preparing the films were also investigated. The prepared films resulted in skinned porous membranes. Results showed that films prepared from pre-treated PLA pellets (dried or melted pellets) did not improve thermal properties and thermal stability compared to films prepared from pure PLA pellets. Considering the aspect of drying, no remarkable differences observed between films dried in an conventional oven and films that were further dried in a vacuum oven after being dried

in an oven in terms of the thermal stability i.e. removal of water and DMSO solvent. However in terms of structure, films dried in a vacuum oven were found to have collapsed whereas the films dried in a conventional oven showed surfaces with continuous flat features.

Only small differences in thermal properties were detected between films immersed in water or 50/50% water/MeOH non-solvent baths. Films immersed in water as a non-solvent displayed higher thermal stability compared to films immersed in 50/50% water/MeOH. Films immersed in 50/50% water/MeOH showed relatively lower thermal stability because of lower infinity in Henson parameters between the PLA-water/MeOH compared to PLA- water in addition to characteristics of MeOH liquid as non-solvent which contribute to reduce thermal and chemical stabilities.

Compared to the film prepared at 5% PLA concentration from pure pellets, the film prepared at 10% PLA concentration exhibited higher thermal properties and stability in addition to having a controllable viscosity for casting. Above all, the film prepared at 10% PLA concentration using pure PLA pellets and immersed in water with conventional oven drying presented the optimum preparatory conditions despite the film suffering from shrinkage. Therefore, the preparatory conditions for the fabrication of this film was implemented further to improve and optimise its morphological structure.

Reducing the initial casting thickness led to substantial improvements on the film microstructure structure besides overcome the issue of shrinkage. The physical properties were measured for films fabricated at varying initial casting thicknesses. Results obtained from DSC and XRD analysis confirmed that the crystallinity of films decreased with decreasing casting thickness. The thermal properties and thermal stability approximately remains the same for all fabricated films. In term of

microstructure, SEM images indicated that films fabricated at 150 μm , 100 μm and 50 μm resulted in continuous pore channels consisting of finger-like microstructures while a sponge-like structure without continuous pore channels was observed for the film with 25 μm casting thickness. Films fabricated with a casting thickness of 50 μm and 25 μm formed uniform films with no shrinkages observed in their structures, however the 25 μm film suffered from brittleness in its structure. The quick phase exchange between the solvent and non-solvent and thus led to produce films with no shrinkages sufferers. Considering the results and observations, the film casted with a thickness of 50 μm has the most optimum properties in term of microstructure, surface morphology and physical dimensions for fabrication.

Chapter 5: Fabrication of Hybrid Poly Lactic Acid/Metal Organic Framework Films: Mixed Matrix Membranes

5.1 Introduction

Polymeric materials have been widely investigated in various applications such as membrane technology for both gas and liquid applications. Polymeric membranes are cheap, durable and flexible to process and fabricate (Chung *et al.*, 2007). On the other hand, they exhibit low thermal and chemical stability, low selectivity and fouling issues (Chung *et al.*, 2007). Inorganic and hybrid materials such as zeolites and MOF materials have high selectivity and the ability to operate at high temperatures; however they are expensive and difficult to process, especially on a large scale (Ismail and David, 2001, Li and Yang, 2008).

To overcome the disadvantages of polymeric and inorganic materials, attention has shifted towards composite MMMs which are able to utilise the advantage of both aforementioned materials. In general, MMMs are comprised of inorganic materials dispersed in a polymeric matrix. The adhesion of the polymer phase and the inorganic material is dependent on the fabrication parameters of MMM (Muntha *et al.*, 2017). Similar techniques in fabricating polymeric membranes can be applied for the fabrication of MMMs. Particle aggregations and the particle-polymer interface are one of the most common challenges associated with MMM fabrication (Moore and Koros, 2005). One methodology to reduce the issue of particle aggregation is to initially mix the inorganic particles in the solvent with the addition of a small percentage of polymer before subsequently adding the rest of the polymer to the dope solution after the particles are appropriately mixed (Aroon *et al.*, 2010, Bastani *et al.*, 2013). In helping and improving the interfacial interaction between inorganic particles and the polymer, inorganic-organic hybrid materials i.e. MOFs can be implemented due to the presence of organic linkers (Bae *et al.*, 2010, Elangovan *et al.*, 2012).

Manufacturing novel porous MMMs such as PLA/MOFs can improve the membranes used for liquid separation. Most of the studies regarding MMMs have focussed on the manufacturing of non-porous structures. In this chapter, the effects of incorporating selected MOFs (HKUST-1 and MIL-53) into the PLA matrix is investigated. PLA/HKUST-1 MMMs were fabricated at varying casting thicknesses. Additionally, the effect of immersion time and bath temperature for PLA/HKUST-1 was also investigated. The influence of increasing HKUST-1 loading into PLA matrix was also explored. XRD analysis was used to confirm the stability of MOF structure in the PLA matrix after membrane preparation. SEM imaging was used to investigate the morphology and thickness of the fabricated films. The thermal stability and properties of films were examined by both TGA and DSC analysis. The physical properties were also measured and reported at varying HKUST-1 loadings.

5.2 Fabrication of hybrid PLA/HKUST-1 MMMs

The fabrication conditions selected for pure PLA films in Chapter 4 were considered to fabricate PLA/MOFs MMMs. Hybrid PLA/MOFs MMMs were prepared with 5wt% of HKUST-1 loading on glass substrates and immersed in distilled water bath at; (a) a temperature of 25°C for 10 minutes, 90 minutes and 24 hours, and (b) temperatures of 5°C, 25°C and 40°C for 90 minutes. They were then subsequently dried in an oven set at 40°C for 24 hours.

The PLA/HKUST-1 MMMs were fabricated at casting thicknesses of 150µm, 100µm, 50µm and 25µm to investigate the effects of HKUST-1 incorporation on different casting thicknesses as shown in Figure 5.4. Generally, similar observations made from pure PLA films whereby film morphology improved with decreasing casting thickness was observed for PLA/HKUST-1 MMMs. Shrinkage, surface tension and non-uniform surface structures were obtained for films casted at 150µm and 100µm. Continuous flat sheet films on the other hand were able to be produced at casting thicknesses of 50µm and 25µm. However, the film with a

25 μ m casting thickness exhibited tears as the film was found to be very brittle and soft (Figure 5.1).

Films with initial casting thicknesses of 150 μ m and 100 μ m showed a light blue colour which visually confirms the presence of incorporated HKUST-1. The presence of HKUST-1 in 50 μ m and 25 μ m films were not visually evident due to the lack of light blue colouration. The reason behind this could be due to the varied amount of HKUST-1 in the thicker films (150 μ m and 100 μ m) compared to thinner ones (50 μ m and 25 μ m). Another possible reason could be due to the dispersion of HKUST-1 powder in the immersion bath as a result of thinner films forming faster. The crystal peaks of HKUST-1 obtained from XRD shown in Figure 5.2 confirms the successful incorporation of HKUST-1 into the PLA matrix for a membrane with an initial thickness of 50 μ m. The film with a 25 μ m initial thickness was not considered as it was very brittle and unsuitable for use as a membrane. Therefore, based on the observed morphological structure of the film and the confirmed incorporation of HKUST-1 in PLA matrix through XRD, the membrane with an initial thickness of 50 μ m was selected for further investigations in this study.

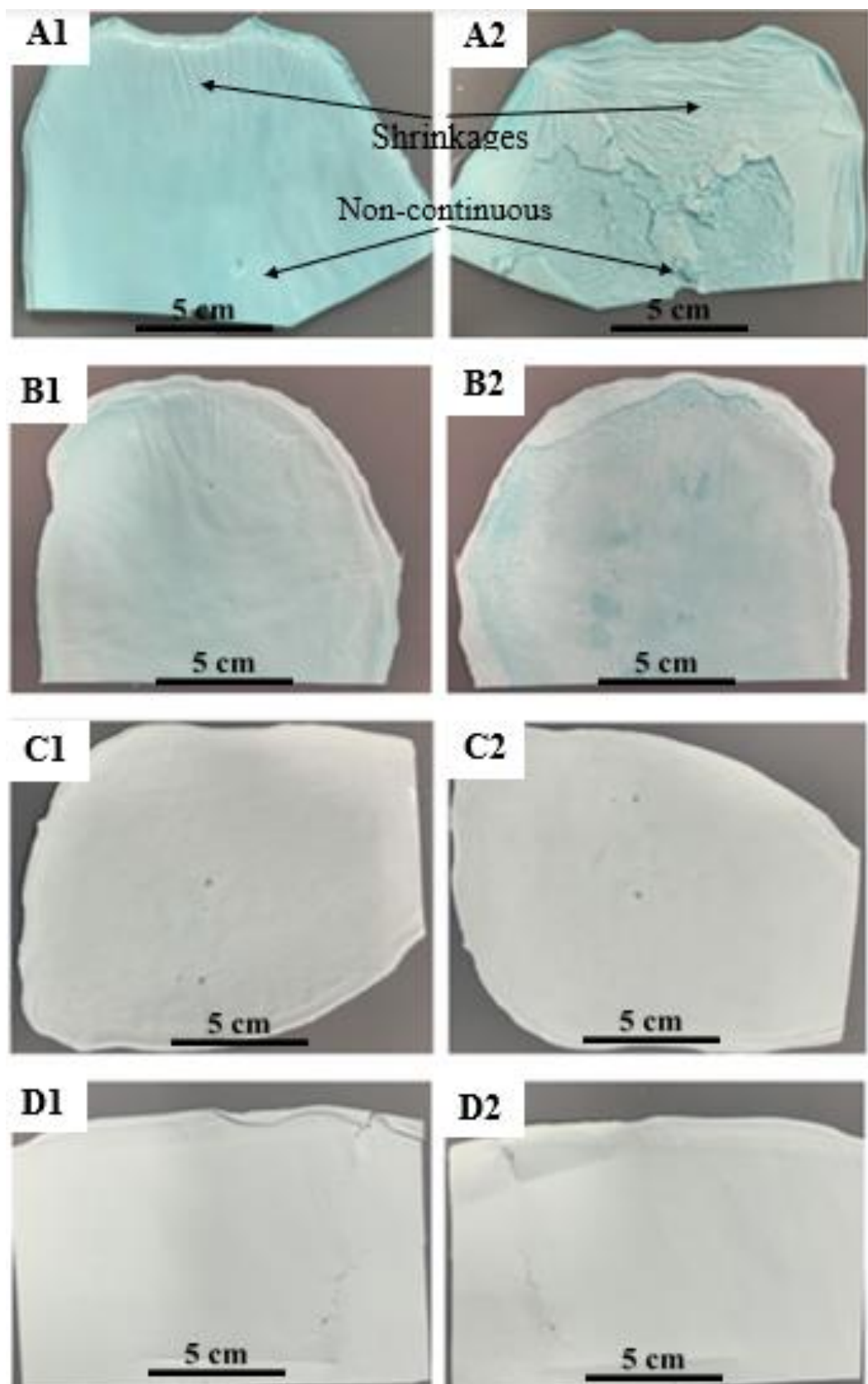


Figure 5.1: Top and bottom sides of PLA/HKUST-1 MMMs casted at varying initial casting thicknesses with 5% HKUST-1 loading. Films were casted on a glass substrate. (A1) top view side of 150 μm film, (A2) bottom view side of 150 μm film, (B1) top view side of 100 μm film, (B2) bottom view side of 100 μm film, (C1) top view side of 50 μm film, (C2) bottom view side of 50 μm film, (D1) top view side of 25 μm film and (D2) bottom view side of 25 μm film.

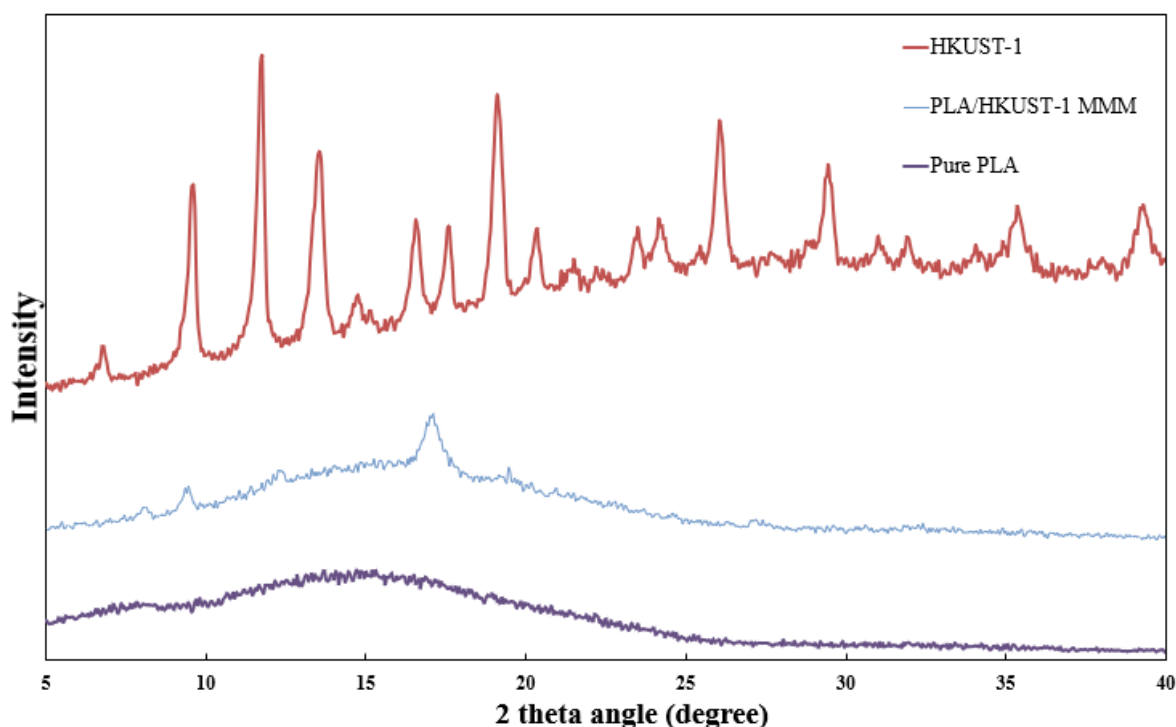


Figure 5.2: XRD data for film crystals from 5° to 40°. Pure PLA and 5wt% HKUST-1 loaded PLA/HKUST-1 MMM were prepared at a thickness of 50µm. The films were immersed at 25°C in a water bath for 24 hours.

5.3 Effect of immersion time

The influence of immersion time for the fabrication of PLA/HKUST-1 MMMs was investigated. The films were fabricated with an initial thickness of 50µm using a 5wt% HKUST-1 loading and immersed in a 25°C bath temperature for 10 minutes, 90 minutes and 24 hours. It was visually observed that the film started to form in approximately 10 minutes; and therefore a 10 minute immersion time was taken into consideration. A 90 minute immersion time was also considered since the film fully forms and leaves the surface of the casting substrate in a time of 90 minutes. A 24 hour immersion time was taken into account as a reference point for comparison between results obtained from the 10 minute and 90 minute immersion times since the films would have been fully formed.

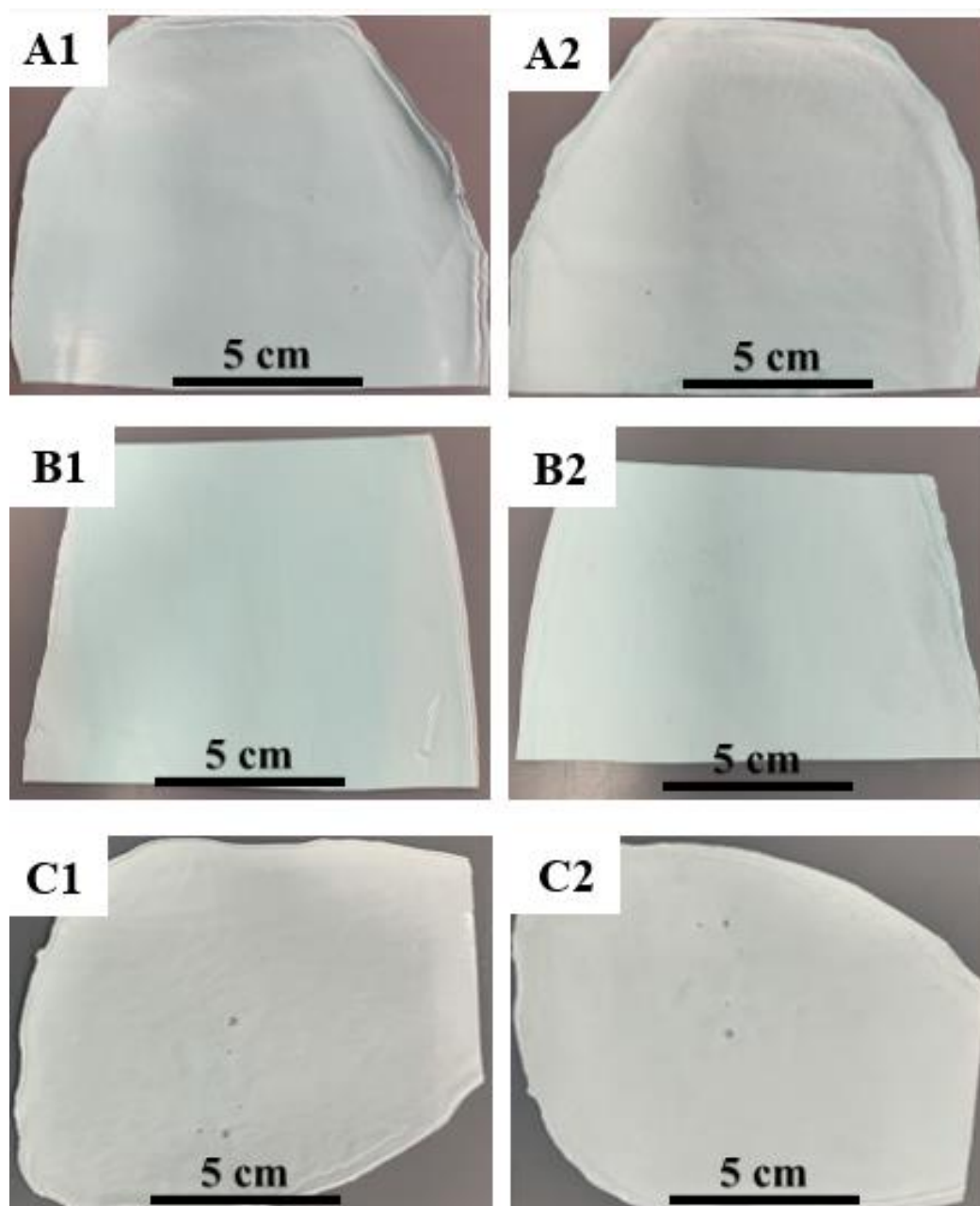


Figure 5.3: Optical top and bottom surface morphology sides of PLA/HKUST-1 MMMs fabricated with 5wt% HKUST-1 loading and an initial thickness of 50 μ m. The films were immersed in water at 25 $^{\circ}$ C for 10min , 90min and 24hr. (A1) top surface morphology of the film immersed for 10min, (A2) bottom surface morphology of the film immersed for 10min, (B1) top surface morphology of the film immersed for 90min, (B2) bottom surface morphology of the film immersed for 90min, (C1) top surface morphology of the film immersed for 24hrs, (C2) bottom surface morphology of the film immersed for 24hrs.

PLA/HKUST-1 MMMs fabricated with a casting thickness of 50 μ m and immersed in a water bath for 10 minutes, 90 minutes and 24 hours are shown in Figure 5.3. Considering the aforementioned figure, the presence and distribution of HKUST-1 particles into the PLA matrix is evident on both the top and bottom sides of the films. It shall be noted here that the top side

is the side in direct contact with the water bath while the side attached to the substrate is the bottom side. No shrinkage was observed among the films and their respective surface morphology was found to be continuous. The films immersed for 10 minutes and 90 minutes exhibited blue colourisations compared to the film immersed for 24 hours. Confirmed by XRD analysis, this indicates that more HKUST-1 was incorporated into the PLA matrix.

XRD measurements were carried out on each film in order to confirm the preservation of the crystal structure of HKUST-1 during membrane preparation. A comparison between the XRD patterns of HKUST-1 powder, pure PLA film and PLA/HKUST-1 MMMs are shown in Figure 5.4. The characteristic peaks of HKUST-1 was determined to be exhibited at 6.8° , 9.6° , 11.7° , 13.5° , 14.6° , 16.6° , 17.6° and 19.1° while the characteristic peak of pure PLA film was determined at 16.9° and 19.1° .

XRD patterns confirmed the presence of HKUST-1 crystals in all MMMs as they exhibited some of the characteristic peaks of HKUST-1. Compared to films immersed for 24 hours, films immersed for 10 and 90 minutes showed relatively larger and clearer peaks for HKUST-1. The films immersed for 10 and 90 minutes exhibited peaks at 6.8° , 9.6° , 11.7° and 13.5° while films immersed for 24 hours showed only small peaks at 9.6° , and 11.7° for HKUST-1. The peak at 19.1° observed for films immersed for both 10 and 90 minutes was most likely a HKUST-1 peak. However, the XRD patterns for the film immersed for 24 hours did not exhibit this particular peak.

From the above, it may be implied that as immersion time increases, the greater the amount of HKUST-1 is loss due to dispersion in the water bath. The non-solvent bath may act as a driver for the diffusion of HKUST-1 in the water bath proportionally with time. This may be a result of the slightly higher density of HKUST-1 (1.58 g cm^{-3}) compared to PLA (1.24 g cm^{-3}) followed by dispersion in the water bath. HKUST-1 may also be loss as a result of the solvent

carrying out some of the HKUST-1 particles from the film matrix into the non-solvent bath during the solvent and non-solvent phase exchange process. As the film stays for a longer period of time in the bath, more HKUST-1 loss occurs. This would explain the darker blue colourisation exhibited by MMMs with shorter immersion times.

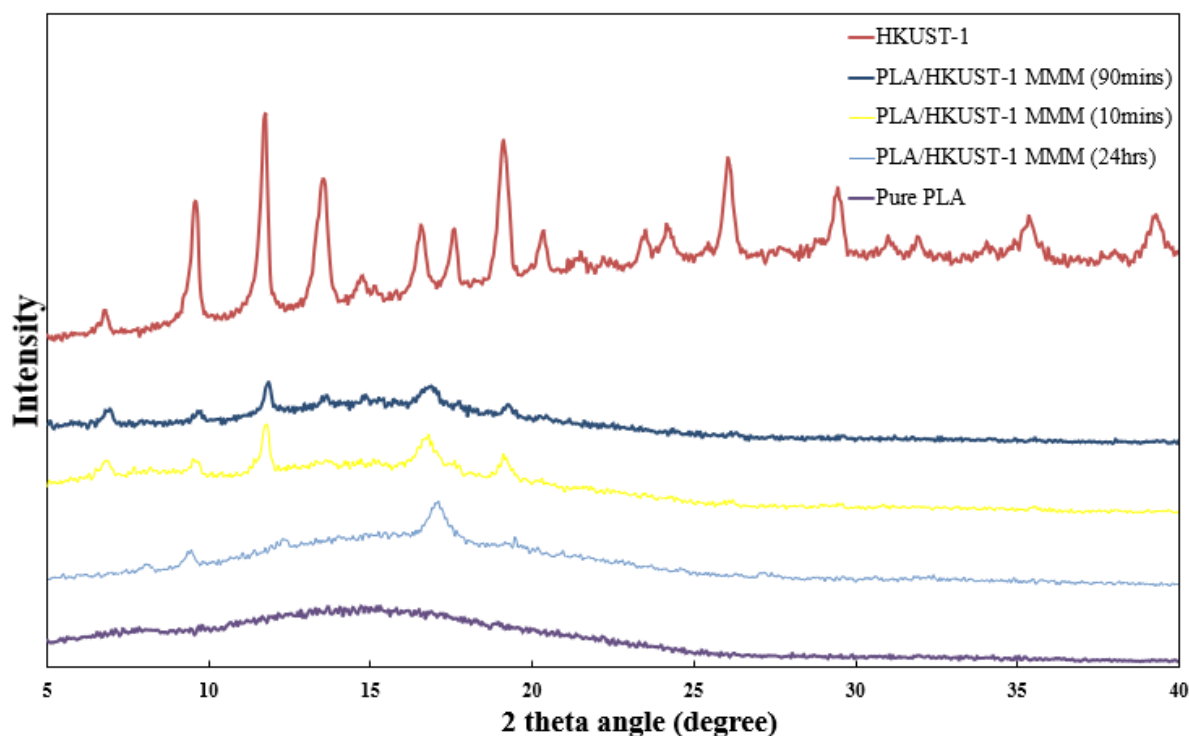


Figure 5.4: XRD data for film crystals from 5° to 40°. Pure PLA and 5wt% HKUST-1 loaded PLA/HKUST-1 MMMs were prepared and casted at a thickness of 50 μ m. The films were immersed at 25 °C in water bath for 10min, 90min and 24hr.

SEM imaging of the cross-section and top view of PLA/HKUST-1 MMMs are shown in Figure 5.5. For all fabricated films, a dense or low porous top layer with the formation of macro-void channels and finger-like structures in their cross-section was exhibited. Furthermore, non-uniform pore sizes and structure were also exhibited. HKUST-1 particles were not clearly seen through SEM imaging and therefore higher magnifications are required to oversee the presence of HKUST-1 particles in PLA/HKUST-1 matrix. Considering Figure 5.5, there are no significant differences in the morphological microstructure of cross-sections between films immersed for 10 minutes, 90 minutes and 24 hours. It shall be noted that the incorporation of HKUST-1 into the PLA matrix did not cause damage to the structure of polymeric films.

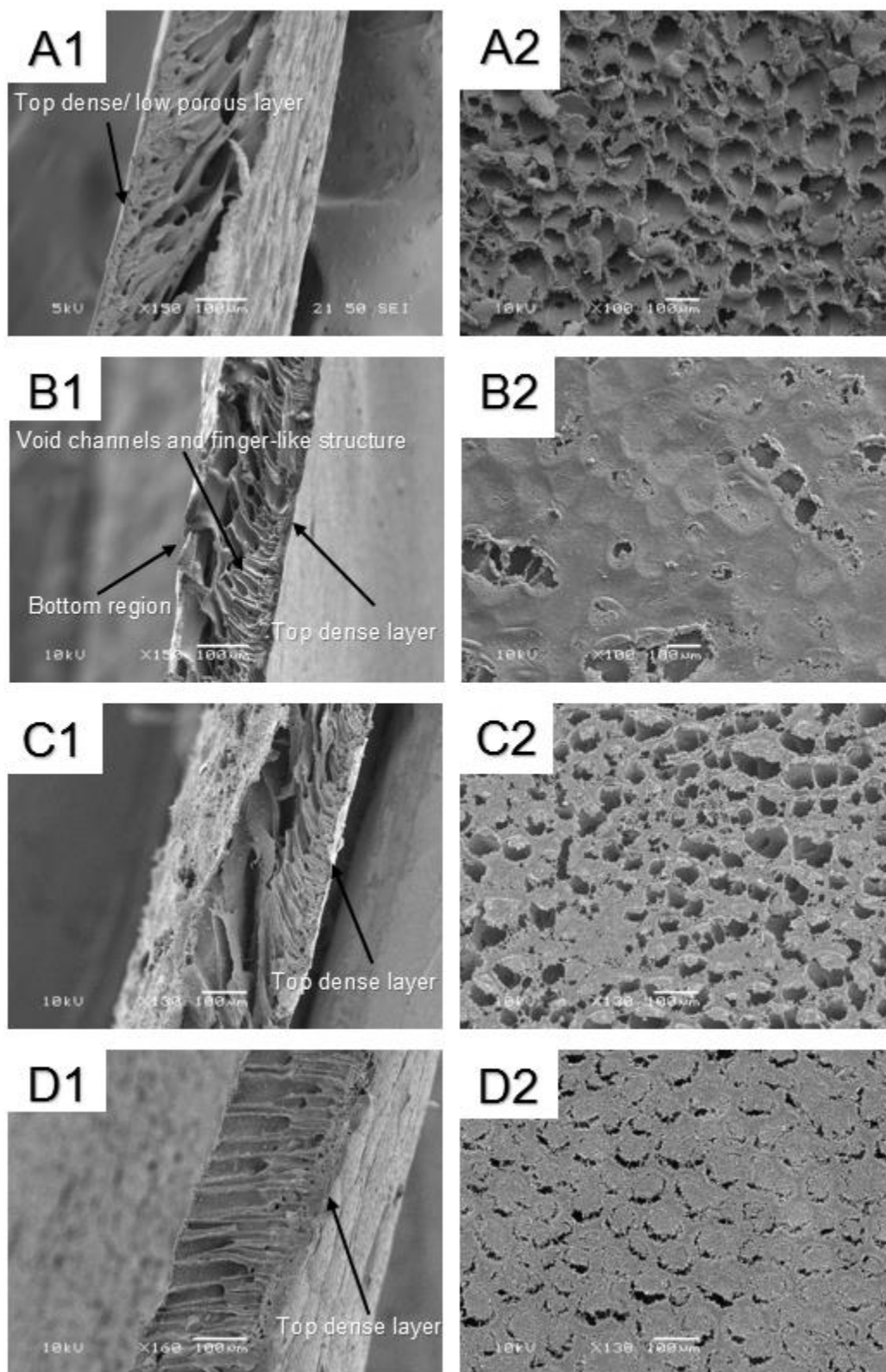


Figure 5.5: SEM imaging of the cross-section and top view of pure PLA film and 5wt% HKUST-1 loaded PLA/HKUST-1 MMMs casted at a thickness of 50µm. PLA/HKUST-1 MMMs were immersed in water bath at 25 °C for different immersion times. (A1&A2)= Pure PLA film immersed for 24 hours. (B1&B2)= PLA/HKUST-1 MMM immersed for 24 hours. (C1&C2)= PLA/HKUST-1 MMM immersed for 90 minutes. (D1&D2)= PLA/HKUST-1 MMM immersed for 10 minutes.

The thermal properties of PLA/HKUST-1 MMMs immersed in 25°C water bath for 10 minutes, 90 minutes and 24 hours obtained from DSC analysis are tabulated in Table 5.1. The results show that the crystallinity of MMMs has a direct relationship with immersion time whereby reductions in immersion time leads to increase in the crystallinity of MMMs. The film has a crystallinity of 8.8% when immersed for 24 hours. When the aforementioned film was immersed for 10 and 90 minutes, the crystallinity increased to 10.2% and 19.0% respectively. The higher crystallinity exhibited by films immersed in shorter periods of time was due to the larger amount of HKUST-1 incorporated into the film matrix. It shall be noted here that the crystallinity of pure PLA films casted with a thickness of 50µm is 8.1% as determined in Section 4.2.2.6 of Chapter 4. As discussed earlier, HKUST-1 is highly crystalline material. Therefore incorporating HKUST-1 into a PLA matrix leads to changes in the crystal structure. The addition of HKUST-1 particles into the PLA matrix may have initiated crystal growth. Hence, the addition of more amounts of HKUST-1 into the PLA matrix results in more contribution and as a consequence more influence on the matrix of the final film in terms of crystallinity. This can be visually observed as it was shown that shorter immersion times lead to films that exhibit a darker blue colourisation compared to longer immersion times, thus indicating more HKUST-1 content. In summary, results show that decreasing the immersion time of PLA/HKUST-1 films during fabrication has no major effect on T_g , T_c , T_m except for crystallinity.

Table 5.1: Thermal properties of the PLA/HKUST-1 MMMs with 5wt% HKUST-1 loading and casted at a thickness of 50µm obtained from first heating. Films were immersed at 25 °C water bath for 10min, 90min and 24hr. Heating was performed from 0 °C to 220 °C using DSC.

Immersion time	T_g (°C)	T_c (°C)	T_m (°C)	χ_{DSC} (%)
24 hours	60.5	92.7	155.6	8.8
90 minutes	60.2	95.7	154.0	10.2
10 minutes	59.9	92.4	152.5	19.0

The thermal stabilities of PLA/HKUST-1 MMMs immersed in a 25°C water bath for 10 minutes, 90 minutes and 24 hours were investigated via TGA with the results being tabulated in Table 5.2. Results show that only one step in weight loss at ~300°C has occurred for all films. Considering Table 5.2, the thermal stability at 5% and 50% showed practically similar values for all fabricated films regardless of the duration of immersion time. From Table 5.2, the percentage of residue at 600°C increased with decreasing immersion times. The percentage residue indicates the presence of HKUST-1 residuals. With this, the increase in percentage residue implies the increase in the amount of HKUST-1 residuals. According to Table 5.2, the film immersed for 10 minutes showed the highest residual contents with a value of 4.5% followed by 4.1% and 3.1% for the films immersed for 90 minutes and 24 hours, respectively.

Table 5.2: Results obtained from TGA analysis of PLA/HKUST-1 MMMs casted at 50µm with 5wt% HKUST-1 loading. The films were immersed in a water bath at 25 °C for 10min, 90min and 24hr.

Immersion time	Thermal stability at 5% (°C)	T_d (°C)	Residue at 600 °C (%)
24 hours	323	357	3.1
90 minutes	326	361	4.1
10 minutes	320	361	4.5

Only small weight loss was detected for water or DMSO which indicates that all films were dried, as demonstrated in Table 5.3. Considering Table 5.3, no significant weight losses at 100°C and 189°C were observed between films immersed at different time periods. At 100°C, there is a weight loss of 0.1% for the film immersed for 24 hours. This is most likely caused by moisture adsorption from the surrounding atmosphere. However, weight loss at 100 °C is 0.5 and 1.1% for the film immersed in 90 minutes and 10 minutes, respectively. This suggests the presence of water residues that are left in the film or in MOF crystals which cannot be removed during drying. In addition to the above, films immersed in shorter periods of time

showed relatively higher weight losses. At 189°C, weight loss increased when immersion time was reduced. The film immersed for 24 hours exhibited a 0.2% weight loss and increased to 0.9% and 1.9% when the films were immersed for 90 minutes and 10 minutes respectively. As discussed previously, shorter immersion time results in films with higher HKUST-1 content in its matrix. Therefore, it is possible that HKUST-1 has adsorbed some DMSO and/or water which could not be easily removed during drying. It is also possible that some moisture and/or other contaminations have been already trapped inside the pores of HKUST-1 before it was incorporated into the film matrix. HKUST-1 is a highly porous material that contains very small pores and therefore it is highly possible that it contained moisture and/or contaminations that did not escape during drying (Duan *et al.*, 2018, Chen *et al.*, 2018).

Table 5.3: Comparison of weight loss at 100°C and 189°C for PLA/HKUST-1 MMMs casted at a thickness of 50µm with 5wt% HKUST-1 loading. Films were immersed in a water bath at 25 °C for 10min, 90min and 24hr.

Immersion time	Weight Loss at 100 °C	Weight Loss at 189 °C
	(%)	(%)
24 hours	0.1	0.2
90 minutes	0.5	0.9
10 minutes	1.1	1.9

In summary, immersion times influences the properties of PLA/HKUST-1 MMMs. Reducing the immersion time led to more HKUST-1 content being incorporated into the PLA/HKUST-1 matrix as was evident from XRD analysis and visually observed from colour changes. Films immersed for 10 minutes and 90 minutes showed more HKUST-1 peaks compared to films immersed for 24 hours thus indicating more HKUST-1 incorporation. In addition to the above, DSC analysis confirmed that crystallinity increases as the immersion time decreases. Results obtained from TGA analysis showed that reduction in immersion time results in more weight loss. In terms of surface structure, the film immersed for 10 minutes were determined to be

more brittle and softer compared to the film immersed for 90 minutes. The film immersed for 24 hours on the other hand did not suffer from any brittleness. With the above, the film immersed for 90 minutes exhibited the optimum incorporation of HKUST-1 in tandem to its film strength and thermal characteristics.

5.4 Effect of immersion bath temperature

The effects of immersion time in the fabrication of PLA/HKUST-1 MMMs were investigated in Section 5.2.2. It was concluded that films immersed in a 25°C water bath for 90 minutes has the most superior film characteristics in terms of HKUST-1 presence, surface morphology, thermal stability and thermal properties. It is therefore considered for further investigations in improving film characteristics.

This section investigates the effect of changing the immersion bath temperature (cold, room temperature, hot) on the fabrication of PLA/HKUST-1 MMMs. The water bath has so far been set to a temperature of 25°C for the fabrication of films. Three different bath temperatures for immersion were selected. The temperature for the cold water bath (5°C) was selected to ensure that water can diffuse just above the water's freezing point into the pores of the film. The temperature for the hot water bath (40°C) on the other hand was selected to be below the glass transition temperature of PLA to avoid any changes in the properties of PLA.

PLA/HKUST-1 MMMs fabricated at a casting thickness of 50µm and immersed in 5°C, 25°C and 40°C water baths for 90 minutes are shown in Figure 5.6. Continuous films without shrinkages or tears were successfully produced for all the films regardless of the immersion bath temperature. However, films immersed in 5°C and 40°C were found to be more brittle and softer compared to the film immersed in a 25°C bath. Incorporation of HKUST-1 into the film matrix may be inversely related with the bath temperature. Figure 5.9 shows that when the bath

temperature was decreased, the resulting fabricated PLA/HKUST-1 film became increasingly blue which corresponds to the incorporation of HKUST-1 as evident from XRD analysis.

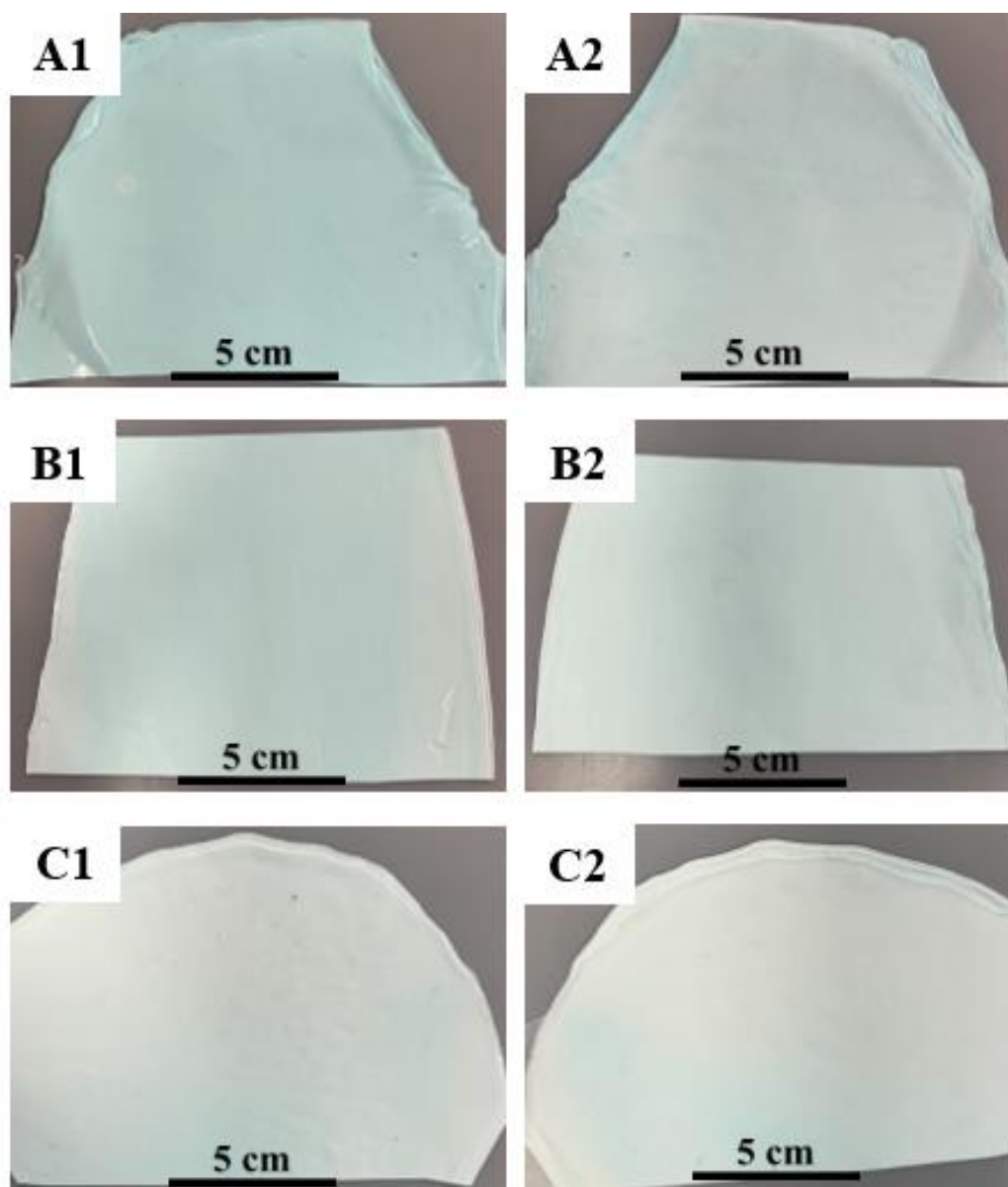


Figure 5.6: Top and bottom sides of fabricated PLA/HKUST-1 MMMs with 5wt% HKUST-1 loading and casted at a thickness of 50µm. Films were immersed in a water bath for 90 minutes and at varying bath temperatures. (A1) top surface morphology of the film immersed at 5°C, (A2) bottom surface morphology of the film immersed at 5°C, (B1) top surface morphology of the film immersed at 25°C, (B2) bottom surface morphology of the film immersed at 25°C, (C1) top surface morphology of the film immersed at 40°C, (C2) bottom surface morphology of the film immersed at 40°C.

XRD patterns films confirming the presence of HKUST-1 particles is shown in Figure 5.7.

HKUST-1 particles were successfully incorporated into PLA matrix regardless of the temperature of the immersion bath. The film prepared at 25°C exhibits a crystal PLA peak at

16.9°. However, no PLA peak(s) were observed for films immersed at 5°C and 40°C bath temperatures. The peak at 19.1° is certainly associated with the crystal structure of HKUST-1 since this peak is exhibited in all the films. An even larger PLA peak was observed for the film immersed in a 25°C bath temperature.

The film immersed in a 40°C water bath showed fewer HKUST-1 peaks compared to the films immersed at 5°C and 25°C. These peaks were observed at 6.8°, 9.6° and 11.7°. The peak at 13.5° visible for films prepared with 5°C and 25°C was missing from the pattern for the film. Considering films fabricated from immersion in a hot bath, HKUST-1 particles may disperse in the water at a relatively higher rate of diffusion due to the high temperature during phase inversion. This most likely led to HKUST-1 particles leaching out of the PLA matrix to be dispersed in the water bath which consequently resulted in low HKUST-1 content for the fabricated PLA/HKUST-1 MMM. To opposite effects, the film immersed in cold water bath at 5°C showed relatively higher HKUST-1 incorporation due to the low rate of diffusion. Tiron *et al.* (2017) fabricated PSf porous membranes with a water immersion bath at temperatures of 5°C, 20°C and 40°C. They concluded that a faster removal of solvent from the polymer solution was observed as a result of accelerated diffusion exchange by water when the temperature of the bath was increased. The membranes fabricated in the study were determined to have exhibited larger and irregular pores, as confirmed by their flux and solute rejection results. The absence of PLA peak(s) at 16.9° for films immersed using 5°C and 40°C baths indicate structural damage or structural changes in the PLA's crystal. This is most likely associated to changes in crystallinity, particularly with the film fabricated at 40 °C film since the immersion temperature is close to T_g , ~60 °C.

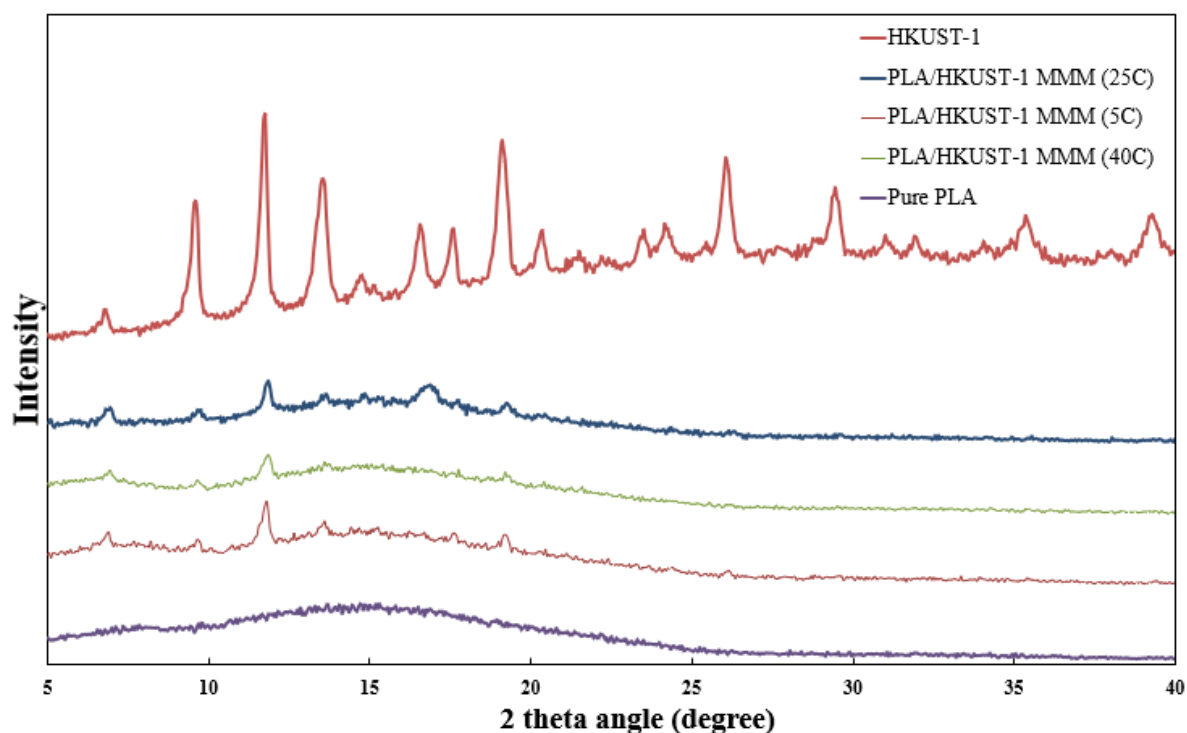


Figure 5.7: XRD data for film crystals from 5° to 40°. Pure PLA and 5wt% HKUST-1 loaded PLA/HKUST-1 MMMs were prepared with a thickness of 50 μ m and immersed in a water bath for 90 minutes at 5°C, 25°C and 40°C.

SEM imaging of the cross-sections of the MMMs fabricated with 5wt% HKUST-1 loading and immersed in 5°C and 25°C show that these films have more continuous pore channels compared to the film immersed at 40°C (Figure 5.8). Surface images showed that films immersed at 5°C and 25°C exhibited pores. However, no visible pores were observed for the film immersed at 40°C. The low immersion temperature of 5°C resulted in a low diffusion rate which caused a thick region of solid aggregation on the surface during film formation. On the other hand, the relatively high immersion temperature of 40°C caused damage in the structural channels of the pores. Madaeni *et al.* (2012) investigated the effect of immersion temperature on the preparation of PES ultrafiltration membranes. Their study showed that at a low immersion temperature of 11°C, the membranes exhibited a small pore sizes with low water flux whereas films immersed at 20°C and 30°C had higher water fluxes. This would imply that higher water flux as a result of immersion in a hot bath, 40°C leads to poor film selectivity/rejection efficiency. The film immersed in cold bath at 5°C on the other hand would be characterised

with higher selectivity but very poor flux. Thus, it is therefore a trade-off between selectivity and water flux.

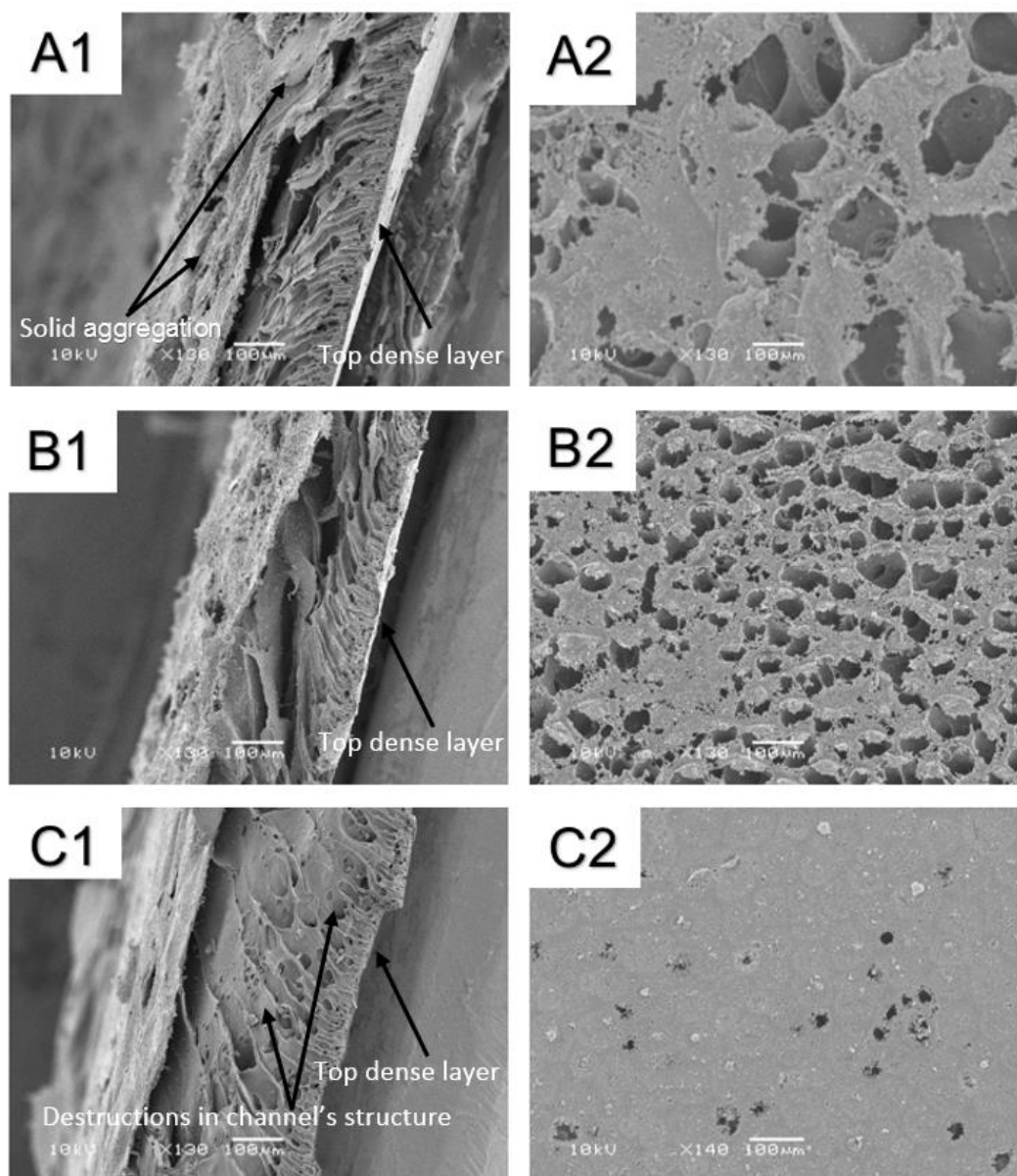


Figure 5.8: SEM imaging of the cross-section and top view of PLA/HKUST-1 MMMs casted with a thickness of 50µm with 5wt% HKUST-1 loading. Films were immersed in 5°C, 25°C and 40°C water bath for 90 minutes. (A1&A2)= film immersed at 5°C bath. (B1&B2)= film immersed at 25°C bath. (C1&C2)= film immersed at 40°C bath.

The thermal properties of fabricated MMMs casted at a thickness of 50µm with 5wt% HKUST-1 loading and immersed in 5°C, 25°C and 40°C water baths for 90 minutes obtained from DSC is summarised in Table 5.4. Results showed that varying the temperature of the immersion bath in the range of 5-40°C has no significant effect on T_g , T_c , T_m . In addition to the

above, an increase in crystallinity was determined with reductions in the temperature of the immersion bath from 40°C to 5°C temperature.

Considering Table 5.4, a decrease in T_g was observed when the temperature of the immersion bath was reduced. The film immersed in a 5°C bath has a T_g of 59.8°C while at 25°C and 40°C T_g increased to 60.2°C and 60.6°C respectively. Minor reductions in T_g indicates that the films may contain trapped solvent/moisture, most likely HKUST-1 particles, which results in relatively high polymer mobility and consequently lower T_g . In addition, results obtained from DSC analysis showed that crystallinity decreased as the temperature of the immersion bath was increased. The results obtained from XRD showed more amounts of HKUST-1 incorporation into the film's matrix for films immersed in cold (5°C) and intermediate (25°C) baths thus implying a higher crystallinity. The higher crystallinity produced from the implementation of cold and intermediate immersion bath temperatures was a result of the contribution of HKUST-1 crystals into the final PLA/HKUST-1 MMMs. Emphasising this further, films immersed at 5°C and 25°C exhibited bluer films (as presented in Figure 5.8) thus indicating more HKUST-1 incorporation in the PLA matrix.

Table 5.4: Thermal properties of PLA/HKUST-1 MMMs casted at a thickness of 50µm with 5wt% HKUST-1 loading obtained from first heating. The films were immersed in a water bath for 90 minutes at 5°C, 25°C and 40°C.

Immersion bath T (°C)	T_g (°C)	T_c (°C)	T_m (°C)	χ_{DSC} (%)
5	59.8	94.0	155.3	15.3
25	60.2	95.7	154.0	10.2
40	60.6	96.9	155.2	4.5

Results of thermal stabilities obtained from TGA of PLA/HKUST-1 MMMs fabricated with a thickness of 50µm using 5wt% HKUST-1 loading and immersed in 5°C, 25°C and 40°C water bath for 90 minutes is presented in Table 5.5. Results showed that only one step in weight loss

occurred with a similar trend of curves being observed for all the films. Lower thermal stabilities at 5% and 50% weight loss were shown for films immersed in cold and hot immersion baths compared to the film immersed at 25°C. More particularly, the thermal stabilities at 5% and 50% weight loss for the film immersed in 25°C bath is 326°C and 361°C respectively. The 5% and 50% weight loss were determined to be 316°C and 351°C respectively for the film immersed at 5°C while the weight loss at 5% and 50% for the film immersed at 40°C was determined to be 314°C and 351°C respectively. The low thermal stability associated with the film immersed at 5°C is most likely due to the presence of HKUST-1. With HKUST-1 being a highly porous material, trapped moisture and/or other contaminations i.e. solvents would contribute to reduction in thermal stability. Based on the results obtained from XRD, the film immersed at 5°C bath exhibits the highest incorporation of HKUST-1 compared to other films. In tandem to the above, more HKUST-1 content which led to reductions in thermal stability is a consequent result of the low thermal stability of HKUST-1 compared to neat PLA (Li *et al.*, 2016, Sofi *et al.*, 2019). The low thermal stability of the film immersed at 40°C is associated to its low crystallinity valued at 4.5% as shown in Table 5.4. The film also exhibited an enhanced degradation rate which also consequently caused a reduction in thermal stability. Farah *et al.* (2016) reported that with increasing water temperature, a faster diffusion rate of water in PLA occurs which enhances the rate of hydrolysis and therefore a faster degradation rate of PLA.

Table 5.5: Results of TGA for PLA/HKUST-1 MMMs casted at a thickness of 50µm with 5wt% HKUST-1 loading. The films were immersed in a water bath for 90 minutes at 5°C, 25°C and 40°C.

Immersion bath T (°C)	Thermal stability at 5% (°C)	T_d (°C)	Residue at 600 °C (%)
5	316	351	1.0
25	326	361	4.1
40	314	351	1.1

Weight loss at the boiling points of water (100°C) and DMSO (189°C) of PLA/HKUST-1 MMMs fabricated with a thickness of 50µm using 5wt% HKUST-1 loading and immersed in 5°C, 25°C and 40°C water bath for 90 minutes is presented in Table 5.6. Results show that only slight weight losses were observed, ~0.5-1.3%, at 100 °C and 189°C were thus almost certainly caused by traces of moisture and DMSO. Therefore, this tells that those PLA/HKUST-1 films were successfully dried by using the conventional oven drying.

Table 5.6: A comparison of weight loss at 100°C and 189°C for prepared PLA/HKUST-1 MMMs casted at a thickness of 50µm with 5wt% HKUST-1 loading. The films were immersed in a water bath for 90 minutes and at 5°C, 25°C and 40°C.

Immersion bath T (°C)	Weight Loss at 100 °C (%)	Weight Loss at 189 °C (%)
5	0.9	1.3
25	0.5	0.9
40	0.6	0.9

5.5 Effect of increasing HKUST-1 loading

In previous sections, the parameters that potentially influences the final characteristics of PLA/HKUST-1 MMMs were examined. These parameters include the initial casting thickness, temperature used for the immersion bath and the duration of immersion bath time. Based on the previous results, the optimum parameters for PLA/HKUST-1 MMMs were determined to

be fabricated at an initial casting thickness of 50 μ m and immersed in a 25°C water bath for 90 minutes. With the established PLA/HKUST-1 MMMs fabrication parameters, it is essential to investigate the influence of HKUST-1 loading on the structure and properties of PLA/HKUST-1 MMMs.

PLA/HKUST-1 MMMs were prepared with HKUST-1 loadings of 5wt%, 10wt%, 20wt%, 30wt% and 40wt%. The films fabricated with 30wt% and 40wt% HKUST-1 loadings were found to be not fully formed as evident from Figure 5.9. This suggests that increasing HKUST-1 loading resulted in relatively free spaces between PLA chains which prevents the chains from linking together to form a film.

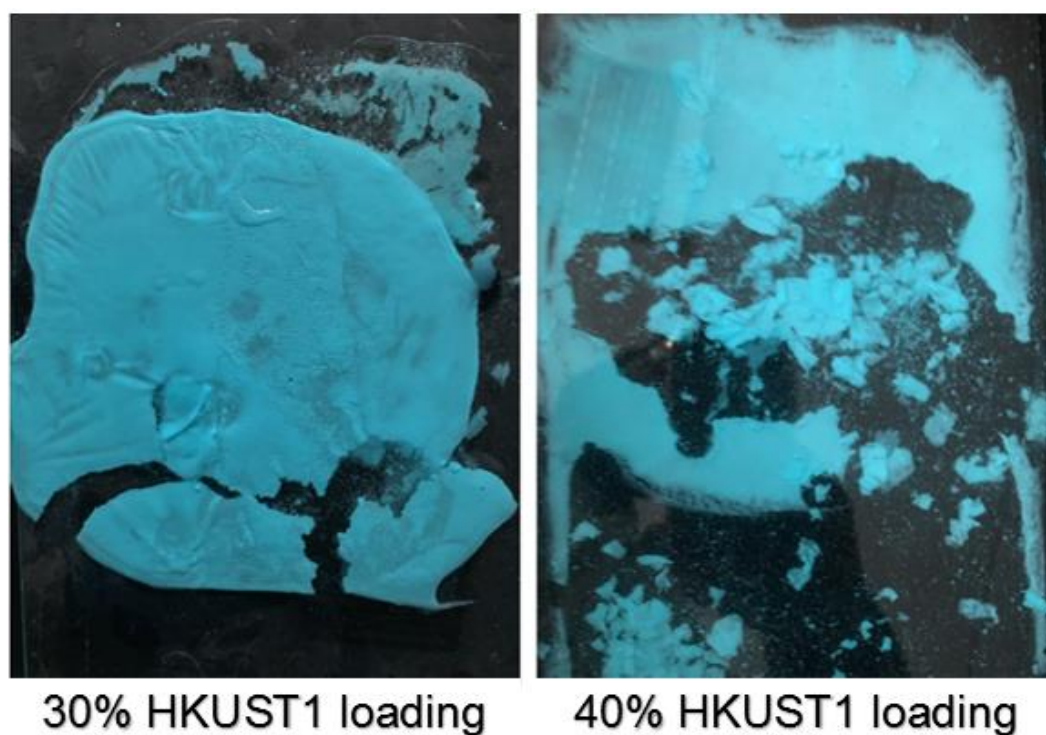


Figure 5.9: Optical surface morphology structure of PLA/HKUST-1 films prepared with HKUST-1 loadings of 30wt% and 40wt%.

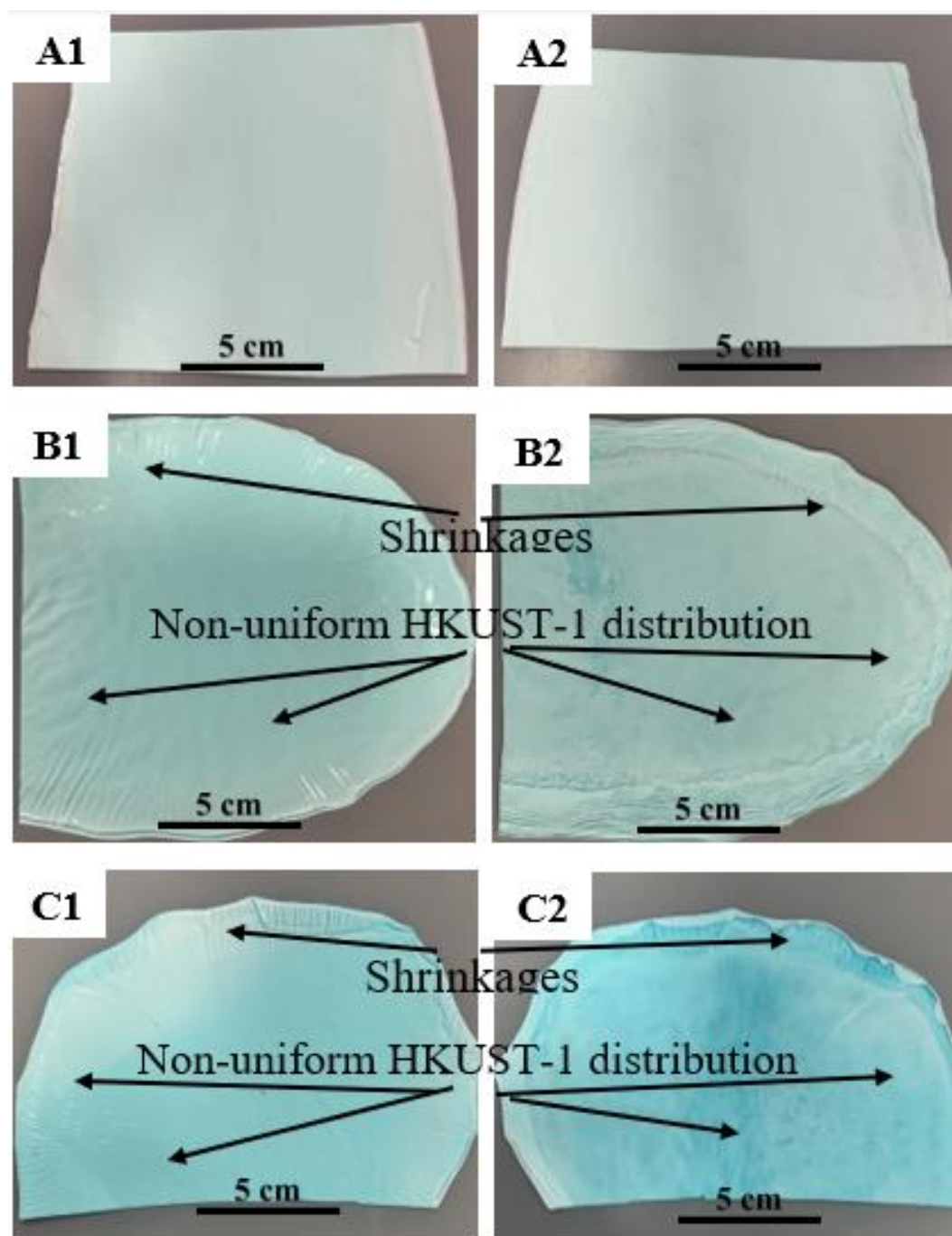


Figure 5.10: Top and bottom optical surface morphology sides of fabricated PLA/HKUST-1 MMMs casted at a thickness of 50 μ m and immersed in a 25°C water bath for 90 minutes. The films were prepared at varying HKUST-1 loadings. (A1) top surface morphology of the 5% HKUST-1 loading film, (A2) bottom surface morphology of the 5% HKUST-1 loading film, (B1) top surface morphology of the 10% HKUST-1 loading film, (B2) bottom surface morphology of the 10% HKUST-1 loading film, (C1) top surface morphology of the 20% HKUST-1 loading film, (C2) bottom surface morphology of the 20% HKUST-1 loading film.

Surface morphological structures of PLA/HKUST-1 MMMs fabricated at a casting thickness of 50 μ m and immersed in a 25°C water bath for 90 minutes at HKUST-1 loadings of 5wt%, 10wt% and 20wt% are shown in Figure 5.10. Based on the pictures in Figure 5.13 the intensity

of the blue colourisation increased as HKUST-1 loading increased from 5wt% to 20 wt% thus indicating more HKUST-1 incorporation in the film. In tandem to this, shrinkage, surface tension and nonhomogeneous were observed with increasing HKUST-1 loading. The distribution of HKUST-1 particles was also observed to be non-uniform as HKUST-1 loading was increased. This may be due to increased HKUST-1 crystal aggregation as the percentage incorporation of HKUST-1 in the PLA increases. This potentially implies that the duration of mixing or the mechanism for mixing are not adequate with the increase in loading.

XRD patterns of PLA/HKUST-1 MMMs fabricated at a casting thickness of 50 μ m and immersed in a 25°C water bath for 90 minutes at HKUST-1 loadings of 5wt%, 10wt% and 20wt% are shown in Figure 5.11. Results obtained from XRD confirmed the presence of HKUST-1 in PLA/HKUST-1 through the characteristic peaks exhibited at 6.8°, 9.6°, 11.7° and 13.5°. HKUST-1 particles were determined to be successfully incorporated into the PLA matrix when the films were fabricated with 5wt%, 10wt% and 20wt% HKUST-1 loadings. In addition, all the films also exhibited crystal peaks of PLA at 16.9° and perhaps 19.1° regardless of HKUST-1 incorporation percentages.

Considering Figure 5.14, results also show that the intensity and number of peaks characteristic of HKUST-1 increased with increasing HKUST-1 loading. The film incorporated with 5wt% HKUST-1 loading exhibited HKUST-1 peaks at 6.8°, 9.6°, 11.7° and 13.5°. Clearer, larger and more peaks were detected for the film prepared with 10wt% and 20wt% HKUST-1 loadings thus indicating more incorporation of HKUST-1 content into the film matrix. The film with 10wt% HKUST-1 loading exhibited HKUST-1 peaks at 6.8°, 9.6°, 11.7°, 13.5°, 16.6°, 17.6° and 26.2°. Additional peaks at 24.5°, 29.6°, 35.5° and 39.5° were exhibited for the film prepared with 20wt% HKUST-1 loading. It is important to note that the particular peak at 19.1° could be associated with either PLA or HKUST-1 or the combination of the two. However, the peak

at 19.1° may be more likely associated with HKUST-1 since the intensity of the peak increased as HKUST-1 loading was increased.

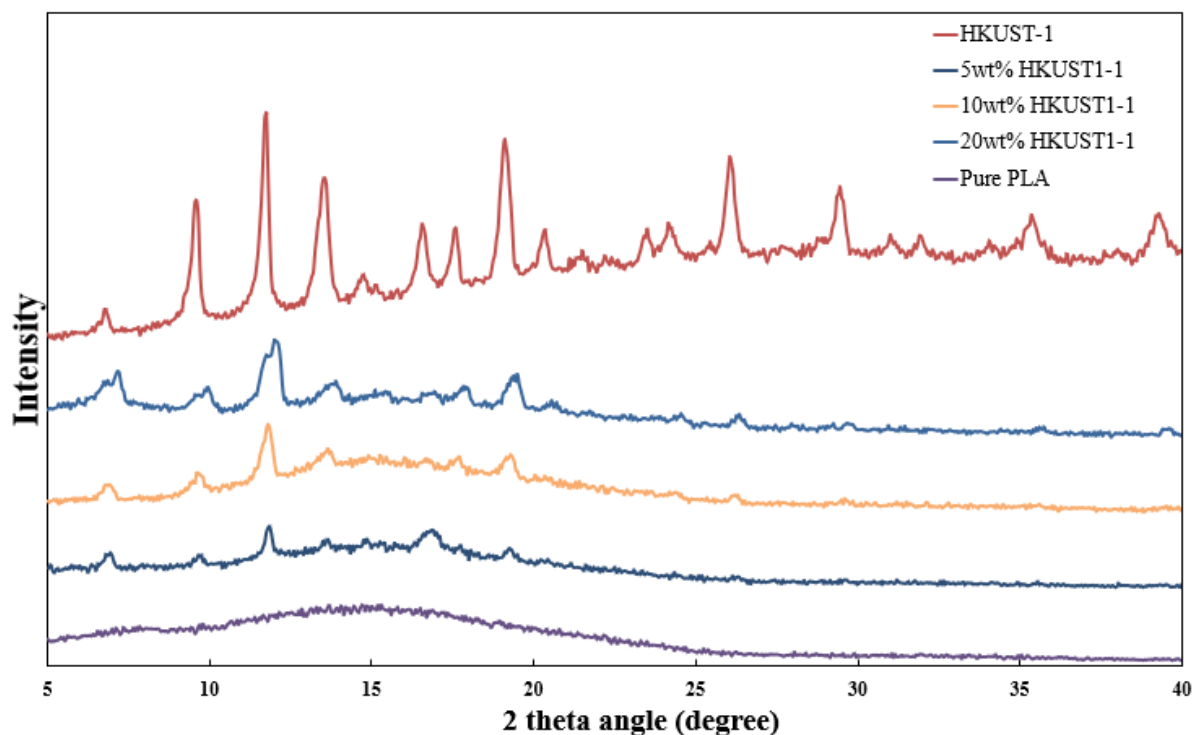


Figure 5.11: Results obtained from XRD analysis of for film crystals from 5° to 40° . Pure PLA and 5wt% HKUST-1 loaded PLA/HKUST-1 MMMs were prepared and casted at a thickness of $50\mu\text{m}$ with 5wt%, 10wt% and 20wt% HKUST-1 loadings.

The morphology of PLA/HKUST-1 MMMs incorporated with 5wt%, 10wt% and 20wt% HKUST-1 are shown in Figure 5.12. SEM imaging shows that asymmetric porous films consisting of a top dense layer and a porous bottom layer are formed at all HKUST-1 loadings. Finger-like structures with pores channels were also formed for all the films. HKUST-1 particles were not easily visually observed despite increase in HKUST-1 loadings.

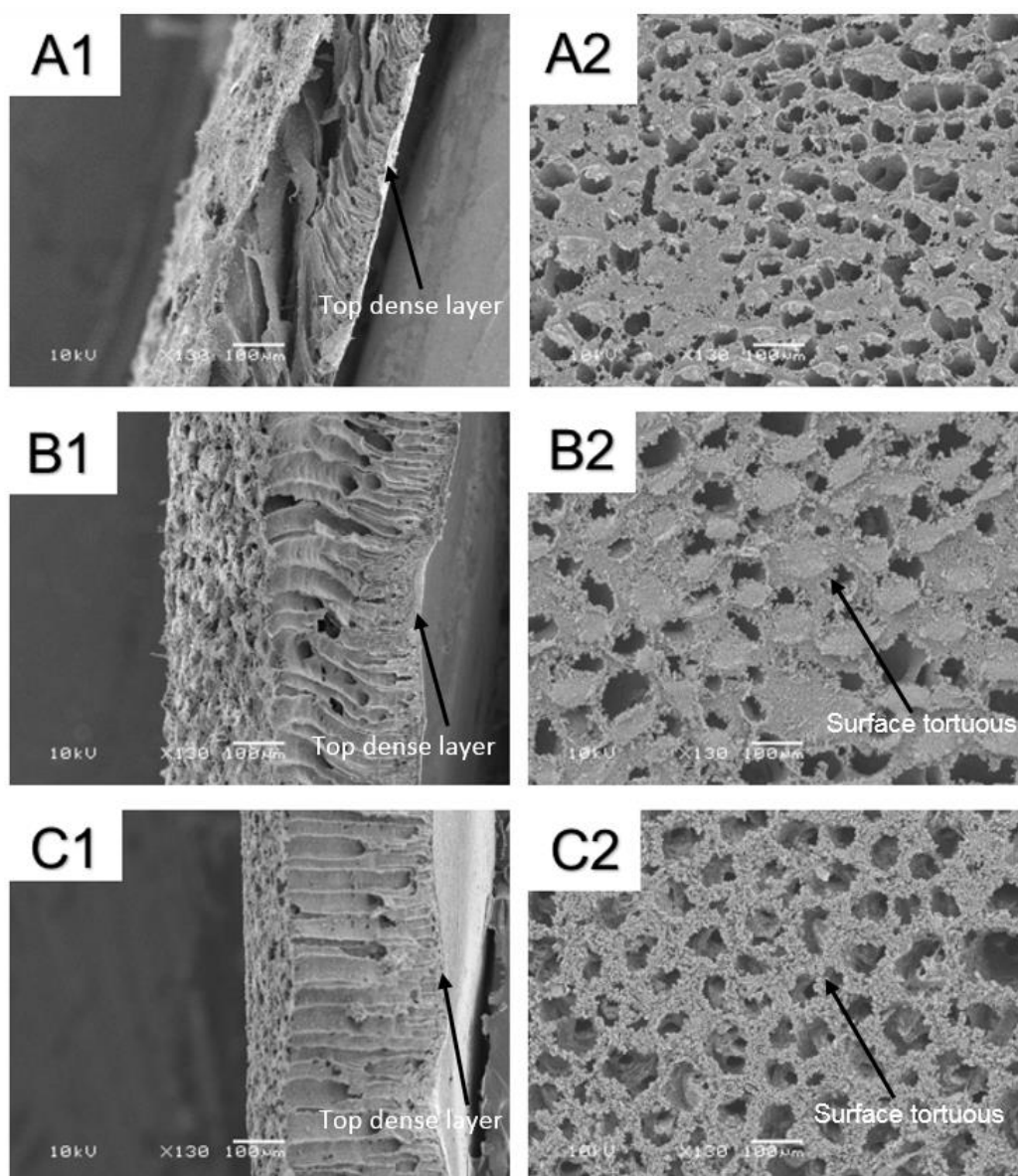


Figure 5.12: SEM images of the cross-section and top view of PLA/HKUST-1 MMMs casted with a thickness of 50µm and immersed in a 25 °C water bath for 90 minutes. Films were prepared at varying HKUST-1 loadings. (A1&A2)= Film prepared with 5% HKUST-1 loading. (B1&B2)= Film prepared with 10% HKUST-1 loading. (C1&C2)= Film prepared with 20% HKUST-1 loading.

Increasing HKUST-1 loading did not affect the structural formation of films with the dense top layer and porous bottom sides along with the pore channels being formed successfully. SEM imaging shows that increasing HKUST-1 loading causes surface tortuosity and HKUST-1 particle aggregation. These particle aggregations consequently precipitate during the phase inversion process. Buonomenna and Golemme (2012) reported the influence of increasing ZIF-8 MOF loading into Matrimid® matrix. The study found that as MOF loading increases, more particle aggregation occurs. With the density of HKUST-1 particles (1.58 g cm^{-3}) being

higher than PLA ($1. \text{ g cm}^{-3}$), precipitation of HKUST-1 particles is highly possible. This is evident from SEM images presented in Figure 5.12 which showed that films fabricated with 10wt% and 20wt% HKUST-1 loading resulted in PLA/HKUST-1 MMMs with more concentrated and darker blue colourisation on the bottom porous side rather than the top side thus implying HKUST-1 precipitation.

Results for the thermal properties of PLA/HKUST-1 MMMs fabricated with 5wt%, 10wt% and 20wt% HKUST-1 loadings obtained from DSC is presented in Table 5.7. The results show that increasing HKUST-1 loading has only minor influences with no observable trends in the results. Overall, the highest thermal properties were observed for the film prepared with 10wt% HKUST-1 loading.

A small increase in T_g was observed as HKUST-1 loading increased. More particularly, the film with 5wt% HKUST-1 loading has a T_g of 60.2°C while the films prepared with 10wt% and 20wt% HKUST-1 loadings have a T_g of 60.7°C and 60.8°C respectively. The proportional increase in T_g with HKUST-1 loading suggests a good interaction between HKUST-1 crystals and PLA chains. This can be implied from previous literature by Kathuria *et al.* (2013) whereby the effects of incorporating various MOF loadings into PLLA to produce a dense matrix was studied. Results of the study showed that increasing MOF loading led to reduction in the mobility of polymeric chains which consequently lead to higher T_g temperature values. Regardless of HKUST-1 percentage incorporation, all the fabricated PLA/HKUST-1 films have approximately matching values for crystallinity which ranges between 10.2-13.9%. The highest crystallinity was exhibited by the film incorporated with 10wt% HKUST-1 loading. This was followed by films prepared with 20wt% and 5wt% HKUST-1 loadings, respectively.

Table 5.7: The thermal properties obtained from first heating for PLA/HKUST-1 MMMs casted at a thickness of 50µm and immersed in a 25 °C water bath for 90 minutes. The films were prepared at 5wt%, 10wt% and 2wt% HKUST-1 loadings.

HKUST-1 loading (%)	T_g (°C)	T_c (°C)	T_m (°C)	χ_{DSC} (%)
5	60.2	95.7	154.0	10.2
10	60.7	97.0	155.3	13.9
20	60.8	92.6	152.5	12.3

The thermal stabilities of PLA/HKUST-1 MMMs fabricated with 5wt%, 10wt% and 20wt% HKUST-1 loadings obtained from TGA are summarised in Table 5.8 and graphically presented in Figure 5.16. Based on the results, no major changes in thermal stabilities is observed with increasing HKUST-1 loading. Considering Figure 5.13, multiple steps in weight loss can be observed for HKUST-1 with major weight loss occurring at 100°C and 300°C. Films with high HKUST-1 loadings of 10wt% and 20wt%, showed significant effects on their weight loss temperature curves obtained from TGA. Low thermal stability at 5% weight loss is observable between 57-143°C. Compared to 5wt% HKUST-1 loaded PLA/HKUST-1, there is an additional weight loss of 4.1%, at 100°C and 189°C. In tandem to the above, increasing HKUST-1 loading produced more residual materials ranging between 1.5-2.8% which corresponds to the accumulation of losses as is expected.

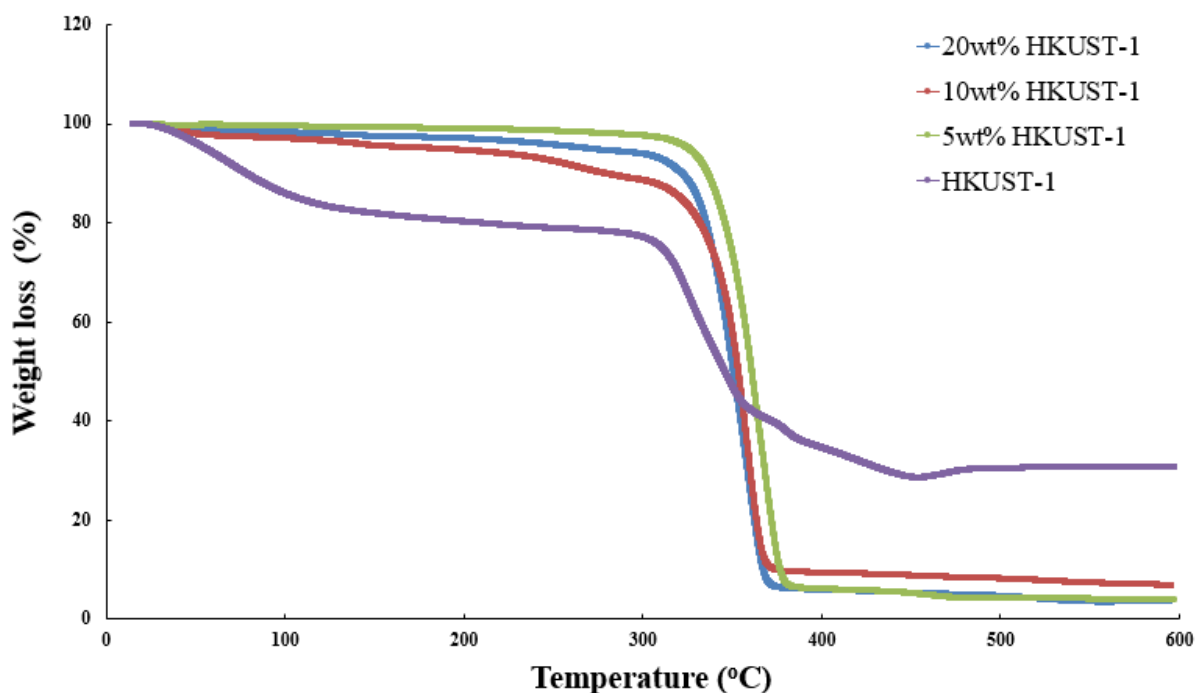


Figure 5.13: Thermal stability of the PLA/HKUST-1 MMMs casted with a thickness of 50 μ m and immersed in a 25 $^{\circ}$ C water bath for 90 minutes. The films were prepared with 5wt%, 10wt% and 20wt% HKUST-1 loadings.

Table 5.8: Results obtained from TGA analysis of the PLA/HKUST-1 MMMs casted with a thickness of 50 μ m and immersed in a 25 $^{\circ}$ C water bath for 90 minutes. The films were prepared with HKUST-1 loadings of 5wt%, 10wt% and 20wt%.

HKUST-1 loading (%)	Thermal stability at 5% ($^{\circ}$ C)	T_d ($^{\circ}$ C)	Residue at 600 $^{\circ}$ C (%)
5	326	361	4.1
10	269	351	5.6
20	183	354	6.9

Considering Table 5.8, the thermal stability at 5% weight loss significantly reduces with increasing HKUST-1 loading. The film fabricated with 5wt% HKUST-1 loading showed a thermal stability of 326 $^{\circ}$ C at 5% weight loss. The thermal stability significantly reduced to 269 $^{\circ}$ C when HKUST-1 loading was increased to 10wt% and subsequently reduced to 183 $^{\circ}$ C when the loading was increased further to 20wt%. This implies that thermal stability with high

weight loss is associated with the HKUST-1 content incorporated in the PLA/HKUST-1 matrix.

Weight loss at the boiling points of water (100°C) and DMSO (189°C) of PLA/HKUST-1 MMMs incorporated with 5wt%, 10wt% and 20wt% HKUST-1 is presented in Table 5.9. From Table 5.9, the amount of weight loss at 100°C and 189°C increased proportionally with increasing HKUST-1 loading. The film incorporated with 5wt% HKUST-1 loading exhibited a weight loss of 0.5% and 0.9% at 100°C and 189°C respectively. The weight losses at 100°C and 189°C increased up to 1.8% and 2.8% respectively as the HKUST-1 loading was increased to 10%. The weight loss further increased to 3.0% and 5.0% at 100°C and 189°C respectively when the HKUST-1 loading increased to 20wt%. This is most likely due to the thermal stability of HKUST-1 particles which consequently influences the final PLA/HKUST-1 fabricated film. Sofi *et al.* (2019) reported that the weight loss occurred during the first stage, approximately 50-125°C, is associated with trapped water and probably solvents i.e. ethanol inside the pores of HKUST-1. Decomposition during the second stage which occurred between 300–400°C is a result of the organic moiety of organic ligands. This involves the decomposition and framework collapse of the HKUST-1 organic linker (BDC =1,4-benzenedicarboxylic acid). HKUST-1 is also a highly porous material and therefore it is possible that it has adsorbed water and/or DMSO into its pores during phase inversion and were not removed during drying. The amount of residue at 600°C increased with increasing HKUST-1 loading thus suggesting increasing amounts of incorporated HKUST-1. This is in agreement with the results obtained from XRD. The residue at 600°C was determined to be 4.1% for the film incorporated with a HKUST-1 loading of 5wt%. The residue however increased to 5.6% and 6.9% when the loading was increased to 10wt% and 20wt% respectively.

Table 5.9: A comparison of weight loss at 100°C and 189°C for PLA/HKUST-1 MMMs casted with a thickness of 50µm and immersed in a 25 °C water bath for 90 minutes. The films were prepared with HKUST-1 loadings of 5wt%, 10wt% and 20wt%.

HKUST-1 loading (%)	Weight Loss at 100 °C (%)	Weight Loss at 189 °C (%)
5	0.5	0.9
10	1.8	2.8
20	3.0	5.0

5.6 Physical properties

PLA/HKUST-1 MMMs prepared with 5wt%, 10wt% and 20wt% HKUST-1 loadings were selected to assess the final thickness, mass, density and porosity. A comparison between the final film thickness and mass of MMMs loaded with 5wt%, 10wt% and 20wt% HKUST-1 and pure PLA film are tabulated in Table 5.10. As discussed previously in Section 4.2.2.7 films swell during phase inversion to form pores and consequently result in the final thickness of the films being higher than the initial casting thickness (50µm). With increasing HKUST-1 loadings, the thickness of the PLA/HKUST-1 films increased correspondingly. Significant increase in thickness can be observed when the film was incorporated with a 10wt% HKUST-1 loading compared to that of the film incorporated with 5wt% HKUST-1 loading. However, only a small increase in thickness can be seen when HKUST-1 loading increased to 20wt%. More particularly, the average thickness of 5wt% HKUST-1 film is $288 \pm 19\mu\text{m}$ while the average thickness of the 10wt% HKUST-1 loaded film is $341 \pm 30\mu\text{m}$. The thickness then increased up to $348 \pm 34\mu\text{m}$ when the film was incorporated with a loading of 20wt% HKUST-1.

In tandem to the increase in thickness, the mass of films also increased with increasing HKUST-1 loading. This is expected since the density of HKUST-1 is higher than PLA and therefore increasing the amount of HKUST-1 in a PLA matrix should correspondingly

contribute to the final mass of PLA/HKUST-1 MMMs. The mass of the film incorporated with a HKUST-1 loading of 5wt% was determined to be 38g.m^{-2} . With the increase in the incorporation of HKUST-1 with 10wt% and 20wt% loading, the mass of the films increased to 44g.m^{-2} and 43g.m^{-2} respectively. The approximately similar value in mass for the two aforementioned HKUST-1 loadings could be due to measurement error or it could be a trade-off point for HKUST-1 percentage incorporation. Based on the increase in film density as a result of increasing HKUST-1 loading, calculations were performed to estimate the real percentage incorporation of HKUST-1. As shown in the Table 5.10, regardless of the initial HKUST-1 percentage incorporation, the actual percentage incorporation of HKUST-1 did not exceed 50% of the initial value for all films. This indicates that the dispersion of HKUST-1 particles in the non-solvent water bath occurred during film formation.

Table 5.10: Actual thickness and mass of pure PLA and 5wt%, 10wt% and 20wt% HKUST-1 loaded PLA/HKUST-1 films casted with a thickness of $50\mu\text{m}$.

HKUST-1 loading (%)	Actual incorporated HKUST-1 (%)	Actual thickness (μm)	Mass (g m^{-2})
0 (Pure PLA)	0.0	293 ± 30	39
5	1.5	288 ± 19	38
10	3.7	341 ± 30	44
20	9.0	348 ± 34	43

A combination of both density and porosity data for PLA/HKUST-1 MMMs fabricated with HKUST-1 loadings of 5wt%, 10wt% and 20wt% is graphically presented in Figure 5.17. As expected, density and porosity have an inverse relationship with each other. Hence, increasing HKUST-1 loading led to the fabrication of films exhibiting higher porosity and lower density, and vice versa. Higher film porosity indicates that the film contains more pores and therefore lower effective density. The opposite also applies where a film with higher density exhibits less porous structure. With considering the influence of increasing HKUST-1 loading into the

PLA matrix this led to slight increases in film porosity and consequently a reduction in the total film density as shown in Figure 5.14. The film fabricated with 5wt% HKUST-1 loading exhibited a porosity of 89.5% which increases to 89.9% and 90.7% as the loading increased to 10wt% and 20wt% respectively. Considering density, the density of the film fabricated with a 5wt% HKUST-1 loading was determined to be 0.132 g cm^{-3} , which then reduced to 0.129 g cm^{-3} for a loading of 10wt% HKUST-1 and further reduced by 0.07 g cm^{-3} when loaded with 20wt% HKUST-1. With the above, it can be implied that increasing the loading of HKUST-1 produces a film structure with more micro voids thus making the film more porous. This therefore suggests that the porosity of the film as well as the pore size is influenced by HKUST-1 loading.

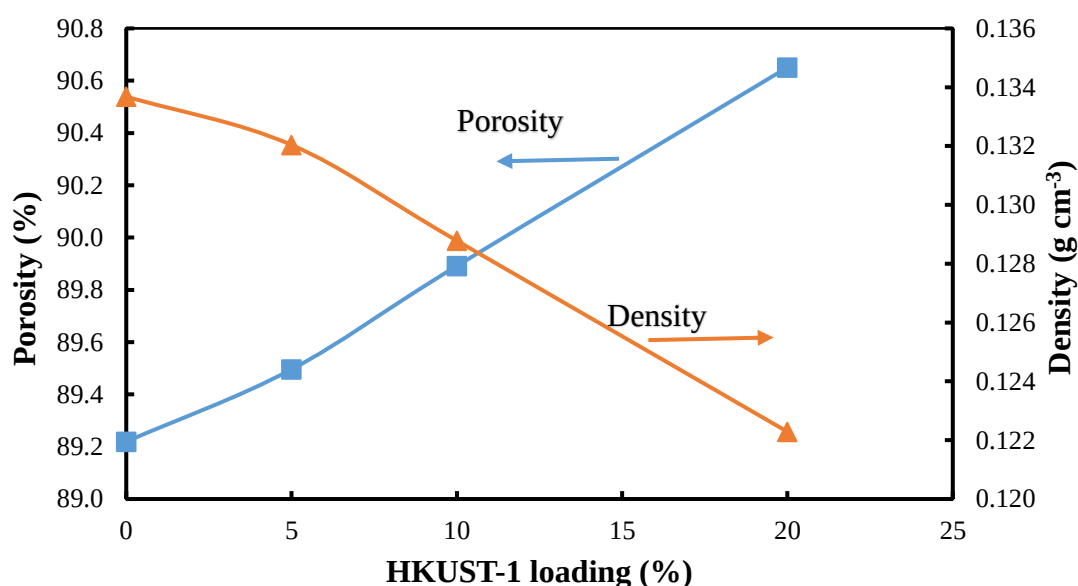


Figure 5.14: Density and porosity measurements of pure PLA and 5wt%, 10wt% and 20wt% HKUST-1 loaded PLA/HKUST-1 films casted with a thickness of $50\mu\text{m}$.

5.7 Fabrication of PLA/MIL-53 MMMs

The incorporation of HKUST-1 MOF into PLA/MOF film matrix has been investigated in previous sections. In order to validate that the fabrication technique for MMMs considered in this study has the potential and ability to be applied for different types of MOFs, another type

of MOF will be considered for investigation. In this section, a MIL-53 MOF will be considered and used to be incorporated into PLA/MOF film matrix.

PLA/MIL-53 MMMs were fabricated with 5wt% MIL-53 loading. MIL-53 takes the form of a white coloured powder and therefore its constituency in the PLA matrix cannot be observed visually. Thus, XRD analysis as presented in Figure 5.18 was used to confirm the incorporation of MIL-53 in the PLA matrix. A similar technique implemented during the fabrication of PLA/HKUST-1 was used to manufacture PLA/MIL-53 MMMs. The films were casted on glass substrates before being immersed in a 25°C water bath for 90 minutes. Three different initial casting thickness i.e. 50µm, 100µm and 150µm were examined.

XRD was carried out for each PLA/MIL-53 MMM in order to confirm the incorporation of MIL-53. MIL-53 is a crystalline material comprising of a regular structure as presented in Figure 5.18. The largest MIL-53 peaks are exhibited at 8.9°, 10.4°, 17.3° and 17.9°. Pure PLA2003D is a semi-crystalline polymer with a XRD pattern that mainly has one single crystalline narrow peak with some small amorphous peaks. The peaks for PLA are exhibited at 16.9° and 19.1°. With this, XRD confirms the presence of PLA polymer and that it has not been destroyed or lost its crystalline structure due to phase inversion for films casted with a thickness of 100µm and 150µm. This was however not noted for the film casted with a thickness of 50µm.

Considering Figure 5.15, it can be observed that the crystal peaks become larger and more pronounced with increasing casting thickness thus suggesting increasing amounts of MIL-53 being incorporated into the film matrix and subsequently higher crystallinity characteristic. MMM-MIL53 films casted with thicknesses of 50µm, 100µm and 150µm exhibited peaks at 8.9° and 10.4°. The peak at 19.1° corresponds to PLA while the wide peaks exhibited at 16.9°-17.3° for films with a thickness of 100µm and 150µm are possibly characteristic of both PLA

(16.9°) and MIL-53 (17.3°). The MMM-MIL53 film casted with a thickness of 50µm exhibits an amorphous-like structure with no sharp peaks. Small peaks at 8.9° and 10.4° were however detected thus confirming the incorporation of MIL-53. It is important to note here that the peaks of MIL-53 were small and few since MIL-53 was only incorporated with a loading of 5wt%.

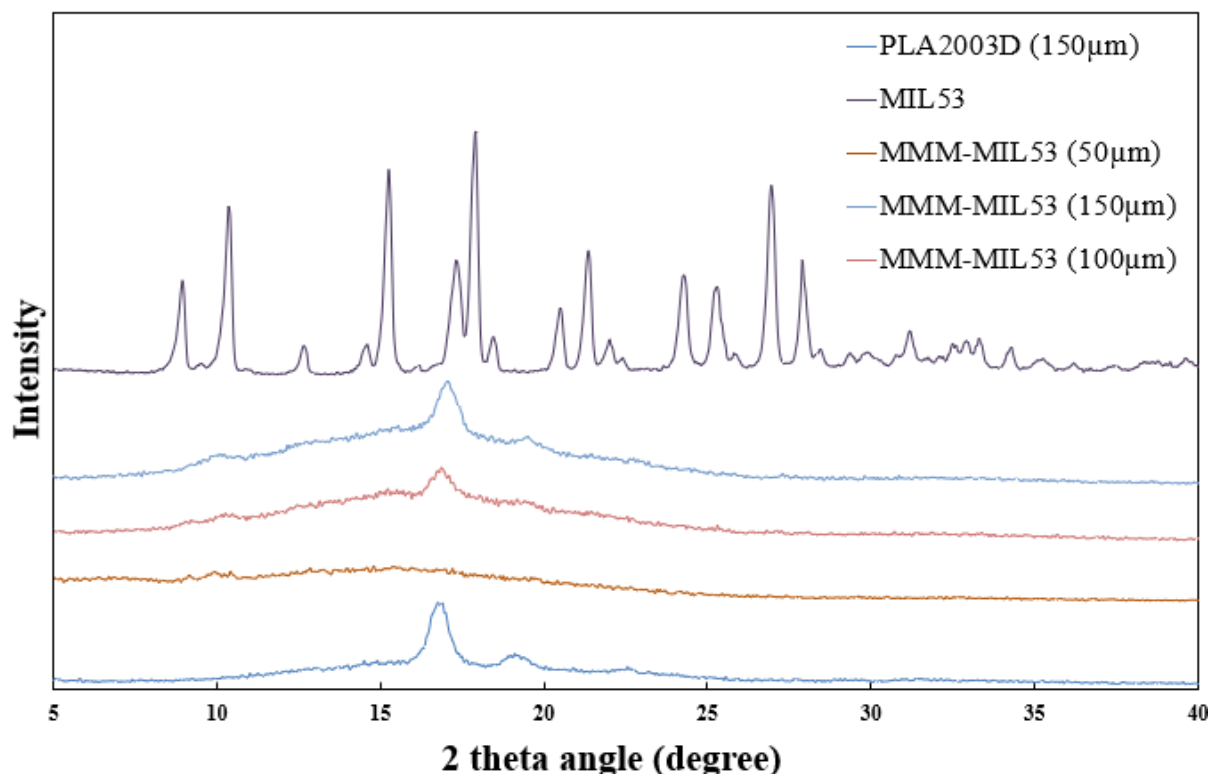


Figure 5.15: XRD data for MIL-53 powder, PLA and PLA-MIL-53 MMM films incorporated with 5wt% MIL-53 loading. Films were casted with thicknesses of 50µm, 100µm and 150µm and immersed in a 25 °C water bath.

5.8 Summary

This chapter has presented the effects of incorporating inorganic materials, particularly MOFs, into a PLA biopolymer to fabricate composite MMMs. Preparatory conditions for the fabrication of porous flat PLA/MOFs MMM sheets via the immersion precipitation technique has been established. The two different types of MOFs considered are HKUST-1 and MIL-53. HKUST-1 was mainly considered and investigated in detail for this chapter. On the other hand, MIL-53 was considered to validate the potential in implementing the fabrication technique used during the fabrication of PLA/HKUST-1 films for different types of MOFs. Based on

performed investigations, PLA/MOFs MMMs were successfully manufactured with MOFs being incorporated effectively.

A 5wt% loading of HKUST-1 was successfully incorporated into PLA matrix to produce PLA/HKUST-1 MMMs. PLA/HKUST-1 MMMs were cast with a thickness of 25 μ m, 50 μ m, 100 μ m and 150 μ m before being immersed in a 25°C water bath for 24 hours. Among the different initial casting thicknesses, a thickness of 50 μ m was established to be the optimum casting thickness to produce continuous flat films that exhibit no shrinkage or brittleness. In addition, the incorporation of HKUST-1 into the film matrix was visually evident based on changes in colour and was analytically emphasised further through XRD.

The duration of immersion in non-solvent bath was adapted to improve the incorporation of HKUST-1 into PLA/HKUST-1 matrix. Films were immersed in a 25°C water bath for three different durations i.e. 10 minutes, 90 minutes and 24 hours. Results showed that the film immersed for 90 minutes exhibited relatively higher thermal stability with less weight loss compared to the film immersed for 10 minutes and 24 hours. The film immersed with a duration of 90 minutes presented the most appropriate thermal properties along with the most suitable strength in surface morphology.

Variations in the temperature for the immersion bath was also explored to assess any potential in improving HKUST-1 incorporation along with the characteristic properties of the fabricated film. PLA/HKUST-1 films were immersed in either a cold (5°C), room temperature (25°C) and hot (40°C) baths for 90 minutes. The maximum amount of HKUST-1 incorporation was then subsequently identified and confirmed for the films immersed in 5°C and 25°C baths via XRD analysis. The film immersed in a 25°C bath exhibited the highest thermal stability and lowest weight loss in addition to their respective validated thermal properties compared to films immersed in 5°C and 40°C baths.

In optimising the parameters for the fabrication of PLA/HKUST-1, PLA/HKUST-1 films were fabricated at varying HKUST-1 loadings between 5-40wt%. PLA/HKUST-1 MMMs were successfully fabricated with HKUST-1 loadings of 5wt%, 10wt% and 20wt% while the film HKUST-1 loaded at 30wt% and 40wt% did not result in formed films. Results showed that increasing HKUST-1 loading led to an increase in the amount of HKUST-1 incorporated into the PLA/HKUST-1 matrix. The thermal properties of fabricated films were not significantly affected. However, a significant reduction in thermal stability along with more weight loss was determined from TGA analysis. The morphological surface structure of fabricated films became brittle and weaker as HKUST-1 loading increased due to the poor interfacial interaction between the PLA and HKUST-1 particles. The physical properties of fabricated films were respectively measured. Results showed that increasing HKUST-1 loading into PLA matrix produced films with higher porosity because of voids formed between the PLA and HKUST-1 which caused as consequence of the poor distribution of HKUST-1 particles into PLA matrix.

Chapter 6: Evaluation of membranes performance and durability

6.1 Introduction

The fabrication conditions for PLA and PLA/HKUST-1 membranes have been discussed and established in Chapters 4 and 5. The controllable parameters that play a big role in influencing the properties and characteristics of films were explored. The fabrication conditions and parameters were then ultimately improved and adjusted in order to produce the most appropriate and optimised porous PLA and PLA/HKUST-1 membranes.

Chapter 4 concluded that membranes prepared from pure PLA pellets at 10wt% PLA concentration and casted with a thickness of 50 μ m before being immersed in a water bath for 24 hours exhibited the most optimised homogenous porous morphological structure without any occurrence of shrinkage or brittleness along with adequate thermal/chemical characteristics. In conclusion of Chapter 5, it was found that the most porous PLA/HKUST-1 membrane is fabricated with 5wt% HKUST-1 loading, casted with a thickness of 50 μ m and immersed in a 25°C water bath for 90 minutes. The parameter for the duration of immersion was initially only studied for the PLA/HKUST-1 membranes thus excluding PLA membranes. To gain consistency for comparison purposes, a PLA membrane fabricated with an immersion time of 90 minutes was considered and fabricated. The results and a brief discussion in regards to the aforementioned fabricated PLA membrane is presented in Appendix 6A. Results concluded that the PLA membrane immersed for 90 minutes has approximately similar properties and characteristics for PLA membranes fabricated with an immersion time of 24 hours. With this, comparisons between PLA and PLA/HKUST-1 membranes fabricated with an immersion time of 90 minutes can be assessed and considered.

In this chapter, PLA and PLA/HKUST-1 membranes loaded with 5wt% HKUST-1 cast with a thickness of 50 μ m and immersed in a 25°C water bath for 90 minutes will be considered to

explore and evaluate their performance and durability. Degradation studies and mechanical properties testing were carefully chosen to evaluate the membrane's durability. In addition, membrane performance was examined by testing water flux and separation performance for selected membranes.

6.2 Mechanical properties

In this experiment, the stress and strain were measured in addition to the Young's modulus and toughness to assess and evaluate the mechanical properties of fabricated membranes. A detailed methodology for mechanical testing has been presented in Chapter 3. In brief, a dog bone shape was cut using a laser cutter with an effective width and length dimensions of 4mm and 11mm respectively. Tensile testing was considered and conducted in a dry condition at room temperature. Testing for each sample was done in triplicates and the average values were reported. For both pure PLA membranes and PLA/HKUST-1 MMMs, a number of membranes prepared at varying initial thickness and immersion times were compared to examine the influence of changing thickness and immersion time on the mechanical properties of membranes. As mentioned previously, the most optimised fabrication conditions for PLA and PLA/HKUST-1 membranes is casting with a thickness of 50 μ m and immersed in a 25°C water bath for 90 minutes. Therefore, PLA/HKUST-1 MMMs with 5wt%, 10wt% and 20wt% HKUST-1 loadings will be compared with pure PLA membrane fabricated using the same conditions.

Results obtained from tensile testing to evaluate the tensile strength, strain at peak stress, elastic modulus and toughness of pure PLA membranes fabricated at varying casting thicknesses and different immersion time are presented in Table 6.1. Considering Table 6.1, no systematic conclusions can be drawn with respect to changes in casting thickness or immersion time. Despite repetitions in tests, the data was observed to be scattered and therefore difficult to

establish strong trends. This thus may indicate that variations in mechanical strength is dependent on casting thickness and immersion time.

Table 6.1: Mechanical properties of PLA films prepared at varying initial thicknesses and immersion time. All the films were immersed in a 25 °C water bath and dried in a conventional oven at 40 °C for 24 hours. The testing for each sample was done in triplicates.

Casting thickness	Immersion Time	Tensile strength (MPa)	Strain at peak stress (-)	Elastic modulus (MPa)	Toughness (kJ/m ³)
150 µm	24 hours	1.43 ±0.06	0.11 ±0.02	39.3 ±9.8	10.26 ±1.78
	90 minutes	1.07 ±0.01	0.13 ±0.02	27.0 ±2.2	9.94 ±2.25
	10 minutes	0.96 ±0.07	0.08 ±0.03	30.4 ±3.1	4.48 ±2.31
100 µm	24 hours	1.28 ±0.14	0.16 ±0.05	32.3 ±7.9	15.61 ±3.13
	90 minutes	1.14 ±0.08	0.16 ±0.04	23.9 ±2.3	11.96 ±3.74
	10 minutes	1.87 ±0.10	0.18 ±0.03	42.5 ±5.1	21.96 ±4.90
50 µm	24 hours	1.61 ±0.05	0.08 ±0.02	60.8 ±12.9	12.07 ±1.12
	90 minutes	1.12 ±0.08	0.06 ±0.01	52.5 ±7.6	7.53 ±1.35
	10 minutes	1.20 ±0.06	0.08 ±0.01	46.7 ±5.5	7.68 ±1.08
25 µm	24 hours	1.43 ±0.12	0.07 ±0.02	65.2 ±8.9	7.32 ±0.38
	90 minutes	1.06 ±0.10	0.04 ±0.01	48.5 ±10.0	3.25 ±0.71
	10 minutes	1.34 ±0.03	0.08 ±0.01	43.5 ±9.5	6.85 ±1.35

Based on the results, it can be seen that membranes casted at 100 µm followed by 50 µm exhibited relatively higher mechanical properties, as compared to membranes fabricated at 150 µm followed by 25 µm. The elastic modulus generally decreases with increasing casting thickness. This may indicate that membranes fabricated at higher thicknesses are less continuous and less uniform. Rezabeigi *et al.* (2014) reported that a more homogenous and continuous morphology leads to higher modulus due to stress transferring and distributing evenly throughout the whole specimen.

Changes in microstructure of the films leads to different mechanical properties. The same study also reported the relationship between elastic modulus and porosity. It was observed that the modulus increases with decreasing porosity for membranes with fragile morphologies. Agreeing to this, in Chapter 4 (Section 4.2.2.7), it was determined that porosity decreases with decreasing casting thickness and here it is established that the modulus increases with decreasing thickness, it can therefore be implied that porosity has decreased. Therefore, this may imply that the aforementioned membranes are not fully uniform and homogenous which would perhaps explain their relatively low mechanical properties. The relationship between elastic modulus and porosity is graphically presented in Figure 6.1. From Table 6.3 it can be seen that toughness increases proportionally with increasing tensile strength. This follows from how a higher toughness indicates more requirement in terms of energy per unit volume before the occurrence of fracture and specimen failure.

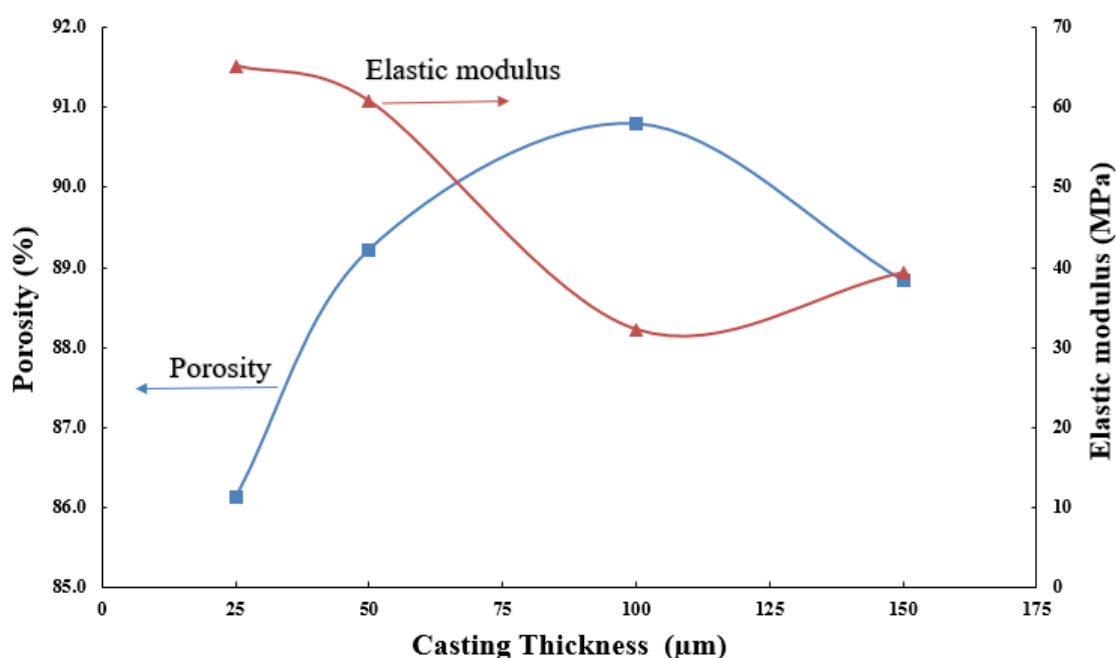


Figure 6.1: The relationship between elastic modulus and porosity as a function of casting thickness. Note that the data is representative of membranes immersed for 24 hours.

The tensile strength, strain at peak stress, elastic modulus and toughness data of PLA/HKUST-1 MMMs fabricated at varying casting thicknesses and immersion times is

tabulated in Table 6.2. Similar to pure PLA membranes, no particular trends can be observed with changes in casting thickness and immersion time. 5wt% HKUST-1 loaded PLA/HKUST-1 MMMs exhibited the same brittle failure mode as pure PLA membranes. In comparison to pure PLA membranes however, it can be clearly seen that PLA/HKUST-1 MMMs exhibit lower mechanical strength which caused as results of the poor adherence between the PLA chains and HKUST-1 particles.

Table 6.2: Mechanical properties of 5wt% HKUST-1 loaded PLA/HKUST-1 MMMs prepared at varying initial thicknesses and immersion time. Films were immersed in a 25 °C water bath and dried in a conventional oven at 40 °C for 24 hours. The testing for each sample was done in triplicates.

Casting thickness	Immersion Time	Tensile strength (MPa)	Strain at peak stress (-)	Elastic modulus (MPa)	Toughness (kJ/m³)
150 μm	24 hours	0.80 $\pm$ 0.03	0.10 $\pm$ 0.01	26.6 $\pm$ 3.6	6.98 $\pm$ 1.05
	90 minutes	0.98 $\pm$ 0.16	0.09 $\pm$ 0.01	30.1 $\pm$ 5.2	4.80 $\pm$ 0.67
	10 minutes	0.86 $\pm$ 0.03	0.08 $\pm$ 0.01	30.7 $\pm$ 3.2	4.37 $\pm$ 0.21
100 μm	24 hours	0.90 $\pm$ 0.03	0.12 $\pm$ 0.01	25.7 $\pm$ 5.2	8.65 $\pm$ 1.44
	90 minutes	1.22 $\pm$ 0.08	0.08 $\pm$ 0.02	37.0 $\pm$ 2.9	9.72 $\pm$ 3.09
	10 minutes	1.01 $\pm$ 0.12	0.06 $\pm$ 0.01	27.6 $\pm$ 2.2	3.65 $\pm$ 1.72
50 μm	24 hours	0.91 $\pm$ 0.06	0.13 $\pm$ 0.01	18.6 $\pm$ 4.5	9.80 $\pm$ 0.52
	90 minutes	0.91 $\pm$ 0.04	0.05 $\pm$ 0.02	39.5 $\pm$ 7.8	3.64 $\pm$ 0.82
	10 minutes	1.02 $\pm$ 0.06	0.04 $\pm$ 0.01	41.6 $\pm$ 2.5	3.68 $\pm$ 0.35
25 μm	24 hours	0.96 $\pm$ 0.06	0.04 $\pm$ 0.01	45.7 $\pm$ 10.0	2.57 $\pm$ 0.46
	90 minutes	1.21 $\pm$ 0.05	0.04 $\pm$ 0.01	49.0 $\pm$ 8.6	4.78 $\pm$ 1.25
	10 minutes	1.17 $\pm$ 0.07	0.05 $\pm$ 0.01	44.7 $\pm$ 12.1	4.72 $\pm$ 0.62

The incorporation of 5wt% HKUST-1 into PLA matrices have reduced the mechanical properties for mostly all the membranes regardless of their initial casting thickness and immersion time. The relative mechanical properties defined in terms of a ratio between PLA/HKUST-1 MMMs and pure PLA membranes fabricated under similar conditions are tabulated in Table 6.3. Nearly most of the membranes prepared under the same conditions have

a MMMs/PLA ratio of $\sim <1$ thus confirming that the mechanical properties of PLA membranes are higher than that of PLA/HKUST-1 MMMs. A few membranes showed ratios of above 1, perhaps as a result of measurement error. This however also indicates that the incorporation of HKUST-1 into PLA matrix has not improved the mechanical properties significantly. In support of the results obtained, Akindoyo *et al.* (2017) studied the influence of adding hydroxyapatite (HA) into a PLA matrix at various HA loadings using injection moulding. Results from the study concluded that the tensile strength reduced for all PLA/HA composites compared to pure PLA in a systematic manner as HA loading increased as a result of poor dispersion and/or low HA strength. In contradiction with results from the current study, Akindoyo *et al.* (2017) reported that the tensile modulus increased proportionally with increasing HA loading due to the higher modulus of HA compared to PLA. The tensile modulus of HKUST-1 and PLA is approximately ~ 10 GPa (Kaskel, 2016, Tian *et al.*, 2018) and 3.5 GPa (Cipriano *et al.*, 2014) respectively. Therefore, it is expected that the addition of HKUST-1 will improve the modulus of fabricated films due to the higher modulus of HKUST-1 compared to PLA as is observed for some films shown in Table 6.3. However, the reduction of modulus for some other films may be associated with film porosity. It has been discussed in Chapter 5 (Section 5.2.5) that the addition of HKUST-1 into PLA matrix has increased overall film porosity. Another possible reason behind the deteriorate in the modulus as the HKUST-1 added into PLA matrix could be due to the weak adherence between the HKUST-1 and PLA and thus led to diminish the overall modulus of the films. The poor distribution of the HKUST-1 particles, non-uniform distribution, within the PLA matrix could also contribute for not to improve the overall modulus of the fabricated films. There are also some potential reasons behind the low modulus of the fabricated films such as the technique used to produce the porous films and the exact characteristics of the type/grade of PLA biopolymer and HKUST-1 used in this study to fabricate the films.

Table 6.3: The relative mechanical properties of 5wt% HKUST-1 loaded PLA/HKUST-1 MMMs to pure PLA membranes (MMM/PLA ratio) at similar preparatory conditions i.e. initial casting thickness and immersion time.

Casting thickness	Immersion Time	Tensile strength (MPa)	Strain at peak stress (-)	Elastic modulus (MPa)	Toughness (kJ/m³)
150 μm	24 hours	0.56	0.91	0.68	0.68
	90 minutes	0.91	0.65	1.11	0.48
	10 minutes	0.90	1.01	1.01	0.97
100 μm	24 hours	0.70	0.74	0.80	0.55
	90 minutes	1.08	0.47	1.55	0.81
	10 minutes	0.54	0.31	0.65	0.17
50 μm	24 hours	0.57	1.64	0.31	0.81
	90 minutes	0.82	0.86	0.75	0.48
	10 minutes	0.85	0.59	0.89	0.48
25 μm	24 hours	0.67	0.56	0.70	0.35
	90 minutes	1.15	1.10	1.01	1.47
	10 minutes	0.87	0.65	1.03	0.69

The influence of HKUST-1 loading on the tensile behaviour of PLA/HKUST-1 MMMs is shown in Figure 6.2. Similar to pure PLA membranes, membranes loaded with 5wt% and 10wt% HKUST-1 exhibited brittle failure mode while membranes loaded with 20wt% HKUST-1 tends to exhibit a ductile failure mode. The influence of mechanical properties for increasing HKUST-1 loading into the PLA matrix is tabulated in Table 6.4. Considering Table 6.6, the incorporation of HKUST-1 into PLA matrix systematically and significantly reduced the mechanical properties. The tensile strength of pure PLA membranes is 1.12MPa decreased down to 0.91MPa, 0.76MPa and 0.48MPa as HKUST-1 was incorporated into PLA matrix with 5wt%, 10wt% and 20wt% loading respectively. It was reported in previous literature that the mechanical strength of PLA composites is dependent on the dispersion of inorganic/organic particles in the PLA matrix (Liuyun *et al.*, 2013). Therefore, it is likely that dispersion is

responsible for reductions in tensile stress as HKUST-1 loading was increased. Šupová et al. (2011) reported PLA suffers from dispersion issues due to poor compatibility and adhesion with some materials. Issues in regards to dispersion can also be associated with possible reductions in the load bearing capacity of PLA-HKUST-1 composites (Sun *et al.*, 2011). In agreement for this, it was established in Chapter 5 (Section 5.4) that increase in HKUST-1 loading resulted in more HKUST-1 aggregation with non-uniform dispersion of HKUST-1 being visually observed in PLA/HKUST-1 MMMs.

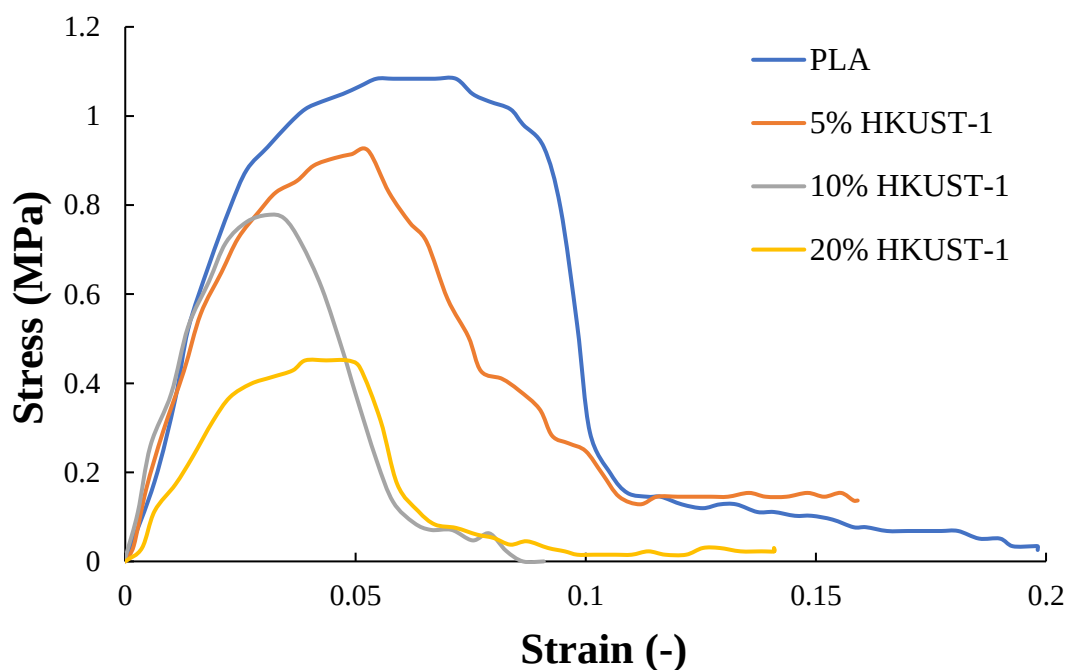


Figure 6.2: Stress-strain graph for pure PLA membrane and PLA/HKUST-1 membranes prepared at 5wt%, 10wt% and 20wt% HKUST-1 loadings. Membranes were casted with a thickness of 50 μ m and immersed in a 25°C water bath for 90 minutes before being dried in a conventional oven at 40°C for 24 hours. Note that the figure is showing representative tests.

Table 6.4: Comparison of the mechanical properties between pure PLA membrane and PLA/HKUST-1 membranes prepared with 5wt%, 10wt% and 20wt% HKUST-1 loadings. Membranes were casted with an initial thickness of 50 μ m, immersed in a 25°C water bath for 90 minutes and dried in a conventional oven at 40°C for 24 hours.

	Tensile strength (MPa)	Strain at peak stress (-)	Elastic modulus (MPa)	Toughness (kJ/m³)
Pure PLA	1.12 $\pm$ 0.08	0.06 $\pm$ 0.01	52.50 $\pm$ 7.6	7.53 $\pm$ 1.35
MMM-HKUST-1 (5%)	0.91 $\pm$ 0.04	0.05 $\pm$ 0.02	39.54 $\pm$ 7.8	3.64 $\pm$ 0.82
MMM-HKUST-1 (10%)	0.76 $\pm$ 0.02	0.03 $\pm$ 0.01	33.19 $\pm$ 10.3	2.49 $\pm$ 0.90
MMM-HKUST-1 (20%)	0.48 $\pm$ 0.07	0.05 $\pm$ 0.01	18.68 $\pm$ 3.5	1.78 $\pm$ 0.63

Elastic modulus and toughness has also significantly reduced as HKUST-1 loading increased. Zuiderduin *et al.* (2003) examined the influence of calcium carbonate (CaCO₃) particles on the toughening of polypropylene. Observation from the study observed some aggregation with brittle failure at high CaCO₃ concentrations. In a different study, Kathuria *et al.* (2013) studied the effects of melt extrusion for the manufacturing of PLA and PLA/HKUST-1 composites on the respective mechanical properties. Results demonstrated that as HKUST-1 loading increased, the mechanical properties which includes tensile strength, elastic modulus and toughness correspondingly decreased. As discussed earlier, it was expected that the addition of HKUST-1 will improve the modulus due to the higher modulus of HKUST-1 (10GPa) compared to PLA (3.5GPa). Reduction in elastic modulus from increasing HKUST-1 loading may be related to membrane porosity. It was discussed in Chapter 5 (Section 5.2.5) that membrane density decreased and the porosity proportionally increased as HKUST-1 loading increased. The relationship between porosity and modulus with respect to HKUST-1 loading is shown in Figure 6.3. It can be clearly seen that the modulus of the membrane correspondingly decreased with the systematic increase in membrane porosity as HKUST-1 loading was increased. In agreement with obtained results, Liao *et al.* (2019) fabricated multi-layered porous PLA specimens of varying thicknesses using 3D printing. Results from the

aforementioned study showed that the modulus consistently decreased as the porosity of the specimens increased. Zenkert and Burman (2009) reported the relationship between density and modulus of polymethacrylimide (PMI) foam. They demonstrated that the density of PMI foam respectively increased the modulus thus emphasising results obtained from the current study further.

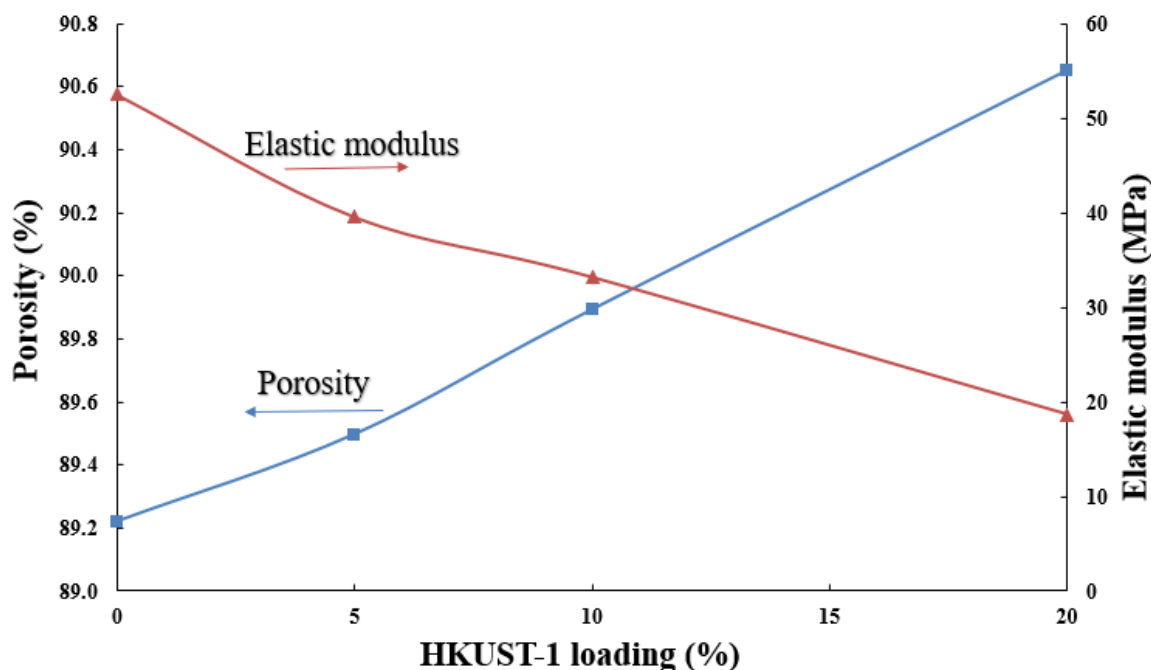


Figure 6.3: The relationship between porosity and modulus as a function of HKUST-1 loading.

6.3 Chemical degradation

With PLA being a biodegradable polymer, a degradation study is needed to explore and assess expected degradation time, or PLA lifetime, of fabricated PLA membranes. The experiment would be very beneficial to determine how long PLA membranes can survive under practical processing conditions before any damage or loss occurs. Due to the long degradation time of PLA, roughly 1-72 months, an accelerated degradation study was considered (Gogolewski, 2000, Gajjar and King, 2014). An accelerated degradation study was performed by immersing PLA specimens in a hot water bath at 50°C. Tensile testing was subsequently used to examine and evaluate the mechanical properties of the PLA membranes at different time intervals. The

PLA membrane used in this experiment is fabricated with the most optimised conditions (cast at a thickness of 50 μ m and immersed in a 25°C water bath for 90 minutes).

The changes in tensile strength, strain at peak stress, toughness and elastic modulus against the degradation time at 50°C are shown in Figures 6.4, 6.5, 6.6 and 6.7 respectively. The rate of PLA degradation was determined to be very high at 50°C and after 77 days, tensile testing was not possible due to the very brittle nature of PLA membranes. With this, only one sample underwent tensile testing and reported at the day 77 while other samples were too brittle for testing. Damaged PLA specimens after exhibiting failure in their respective mechanical structure are shown in Figure 6.8. Based on Figures 6.4-6.7, it can be seen that PLA membranes survived for more than two months before any significant loss or damage occurred. In agreement with obtained results, Karamanlioglu (2013) studied the degradation of PLA coupons with thicknesses of 0.2-0.3mm in a water medium at 25°C, 37°C and 50°C. Results in the study concluded that specimens immersed at 50°C took 48 days for total strength loss from degradation to happen. In addition, approximately ~50% of tensile strength loss was observed after 12 months for the specimens immersed at 37°C while those immersed at 25°C survived for 12 months without any loss in tensile strength.

Overall, some fluctuations in mechanical behaviours can be observed as degradation takes place over time. In addition, a generalised trend for the reduction in mechanical properties, particularly stress, strain and toughness, can be observed as degradation time increased. On the contrary, tensile strength, strain at peak stress, toughness and the elastic modulus stays relatively within the same range with no significant reduction over the entire duration of degradation. In agreement with results in this study, Deroiné *et al.* (2014) studied the relationship between the mechanical properties and degradation time of dense semi-crystalline PLA moulded samples that were immersed in a distilled water bath at elevating temperatures

of 25°C, 30°C, 40°C and 50°C. They found that the elastic modulus remained comparatively similar at all degradation temperatures over time.

In the first few days, between approximately ~3-14 days, a small reduction followed by a significant increase in mechanical behaviours such as tensile strength, strain at peak stress and toughness were observed over time. The PLA2003D is a semi-crystalline grade that contains both crystalline and amorphous chain contents. Therefore, the increase in mechanical properties during the first stage may be associated with the short chains crystallising much more easily than the long chains thus resulting in further crystallisation making the material become slightly stronger while not showing much increase in elastic modulus (Parsons, 2012). In the following degradation stage, the degradation process would continue to take place until the membrane specimens have lost their mechanical strength while exhibiting notable brittle behaviours as observed at day 77.

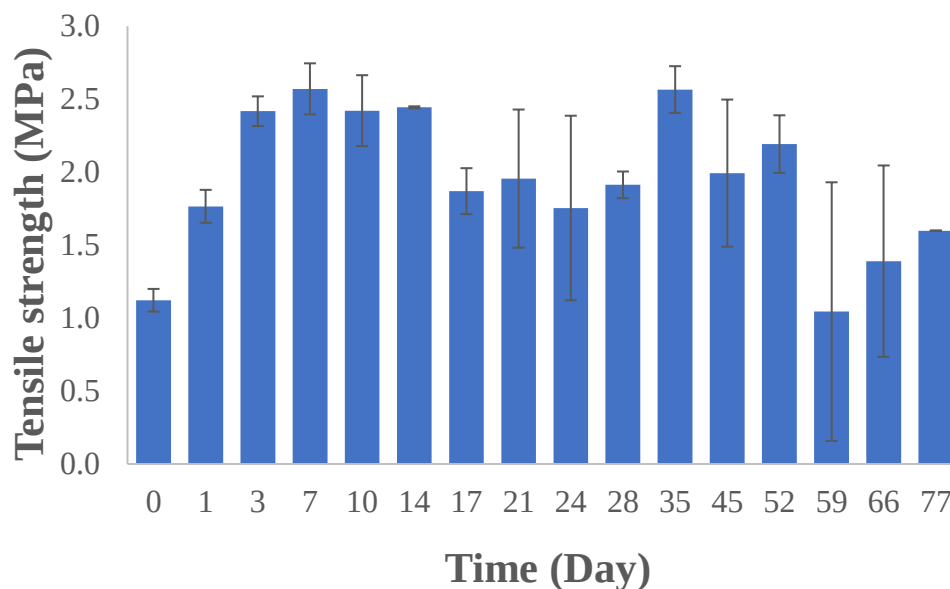


Figure 6.4: Tensile strength data of PLA at different intervals over a 77 day degradation time at 50°C distilled water.

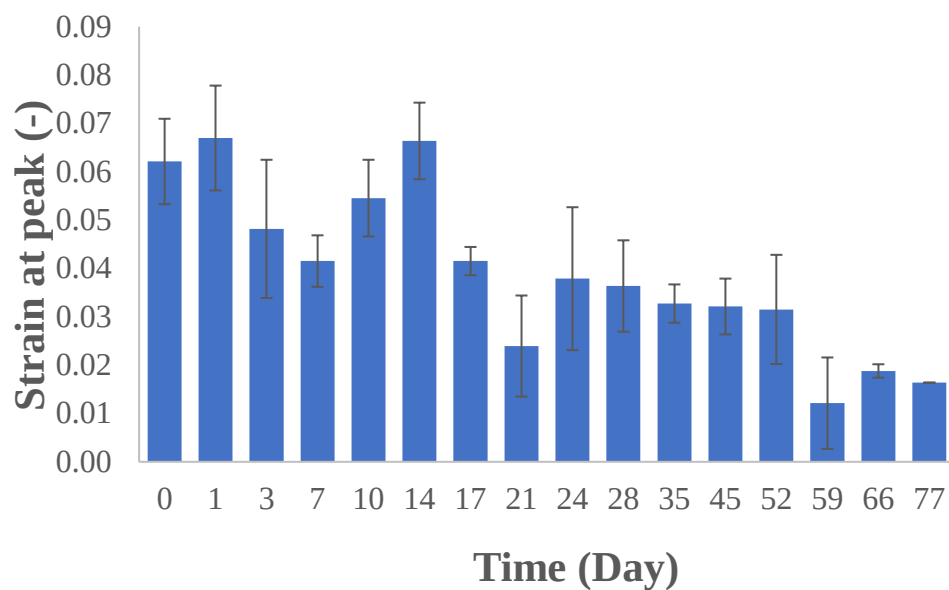


Figure 6.5: Data for strain at peak stress of PLA at different intervals over a 77 day degradation time at 50°C distilled water.

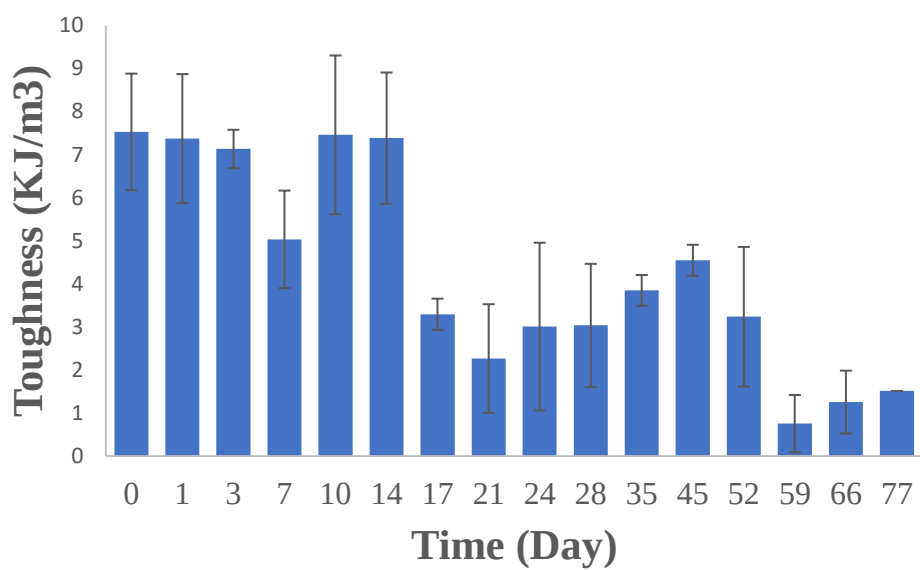


Figure 6.6: Toughness data of PLA at different intervals over a 77 day degradation time at 50°C distilled water.

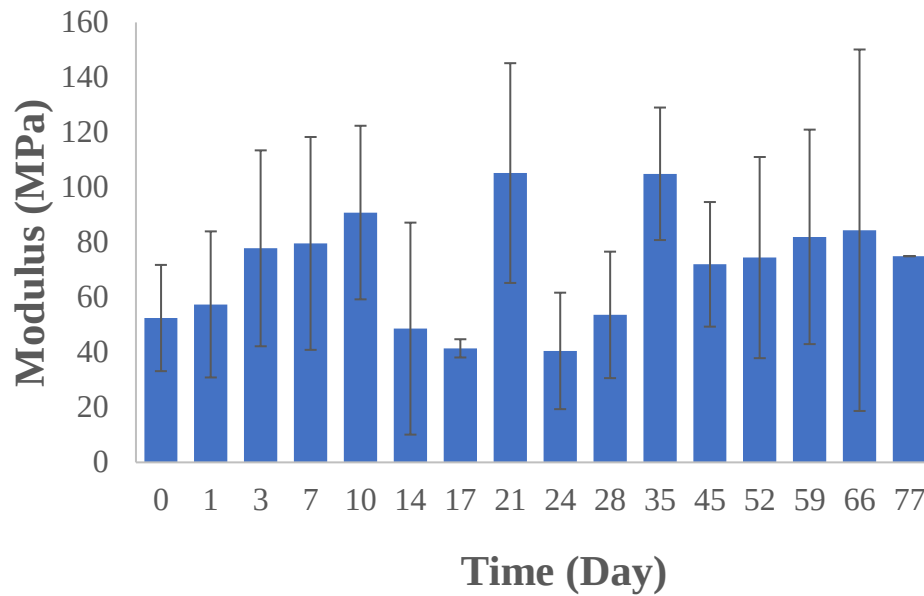


Figure 6.7: Elastic modulus data of PLA at different intervals over a 77 day degradation time at 50°C distilled water.

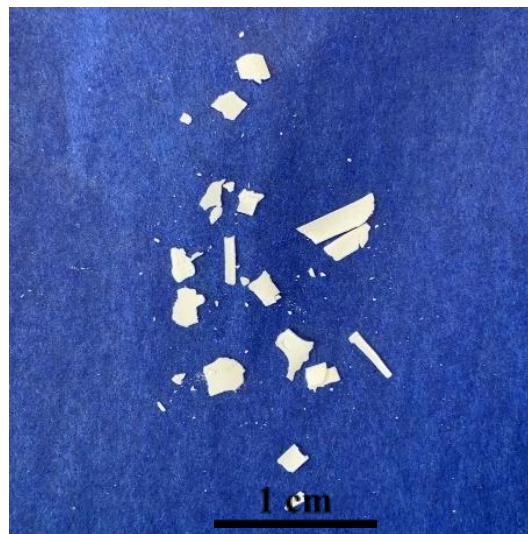


Figure 6.8: Structural damage of PLA specimens after the 77th degradation day.

In performing studies for accelerated degradation, it is essential to estimate the degradation time under actual operating temperature conditions and at room temperature i.e. 25°C for the fabricated membranes. Only a few studies have explored the degradation time of PLA at 25°C with some of those studies considering the usage of different bath mediums for degradation i.e. phosphate buffered saline instead of distilled water. The ratio of degradation temperatures between 25°C to 50°C from the aforementioned studies will be considered for analysis to

predict the degradation time of membranes fabricated in this study at a temperature of 25°C. Deroiné *et al.* (2014) observed a significant loss in mechanical properties of PLA specimens after 15 days when immersed in a 50°C distilled water bath while those immersed at 25°C did not show remarkable changes up to 180 days. Therefore, from the aforementioned study, the required degradation time of PLA at 25°C is at least 12 times longer than at 50°C although it cannot be specified exactly how much longer. Agrawal *et al.* (1997) studied the changes in weight loss of 50:50% PLA-PGA, not 100% pure PLA, in phosphate buffered saline bath at various temperatures. They found that samples take 10-12 times the time needed at 25°C to show a similar impact in degradation at 54°C. With this, results from Deroiné *et al.* (2014) and Agrawal *et al.* (1997) can be taken as a guide to predict the degradation time needed at 25°C before any weight loss and/or loss in mechanical properties occurs in membranes fabricated in this current study. As discussed earlier observations from degradation studies at 50°C found that fabricated membranes survived up to 77 days before any loss in mechanical properties. By taking the factor of 10 as a rough estimation considering the corrected ratio between 25°C and 50°C in terms of degradation time, this thus gives a predicted degradation time of approximately ~770 days (+2 years) for PLA membranes at 25°C. This therefore suggests that PLA membranes fabricated in our study has the ability to survive and operate in water at a temperature of 25°C for more than two years.

6.4 Filtration performance

Studies for pure distilled water flux and particle separation rejections were performed to evaluate the filtration performance for the novel fabricated membranes. This experiment was mainly focussed on pure PLA membranes to explore and evaluate the performance of PLA as a biopolymer material as well as its potential and capability for use in liquid membrane separation applications i.e. water filtration. Pure PLA membranes casted at thicknesses of 100µm, 50µm, and 25µm were studied at various applied pressures of 2, 4 and 6 bar pressures

to examine pure water flux. In addition to this, the operation of membranes at a high pressure was done to inspect the mechanical stability of fabricated bio-membranes under elevated pressure conditions.

According to some prior tests, the experimental procedure in this study was to apply a pressure in triplicates at each 2, 4 and 6 bar pressures for a continuous time of 30 minutes for each membrane considered (see appendix 6B for more details). In other words, each membrane has a total of 9 runs with 3 runs on each applied pressure in the order of 2, 4 and 6 bar pressures. Between each run, the membrane was taken out of the filtration system and immersed in a 25°C water bath in preparation for the next day's run. Particle separation rejection tests were performed for selected pure PLA membranes at 4 bar pressures. Only selected PLA/HKUST-1 MMMs was considered for particle rejection tests.

6.4.1 Pure water flux

Pure water flux of PLA membranes with initial casting thicknesses of 100µm, 50µm, and 25µm operated at 2, 4, and 6 bar pressures are plotted as a function of time in Figures 6.9, 6.10 and 6.11 respectively. In general, all membranes showed a reduction in flux with time regardless of the initial casting thickness. In addition, repetitions of tests (cycle 2, indicated as C2, and cycle 3, indicated as C3) are similar in trend but show only a small reduction in flux with succeeding repeats. For most test runs, the flux started to stabilise and reach a steady state between ~10-20 minutes from the starting time of the test. The same pattern can be observed at different pressures but with a proportional increase in the magnitude of flux as the pressure was increased.

From Figure 6.9 it can be seen that in the first cycles, the water flux was very high before they reduced during the first 30 minutes at all operating pressure conditions. In the second and third cycles, the flux started high but at a lower flux than the first cycle before gradually reducing

and stabilising to reach the steady state. The membrane with a 100 μm initial casting thickness showed a steady state water flux at the end of third cycle at 214 $\text{L.m}^{-2}.\text{hr}^{-1}$ under a 2 bar pressure operating condition, and 364 $\text{L.m}^{-2}.\text{hr}^{-1}$ and 1029 $\text{L.m}^{-2}.\text{hr}^{-1}$ at 4 and 6 bar pressure operating conditions respectively.

Reducing the membrane thickness results in lower water flux as shown in Figures 6.10 and 6.11. The membranes casted at 50 μm showed water fluxes of 64 $\text{L.m}^{-2}.\text{hr}^{-1}$, 279 $\text{L.m}^{-2}.\text{hr}^{-1}$ and 536 $\text{L.m}^{-2}.\text{hr}^{-1}$ at 2, 4 and 6 bar pressures respectively. Further reduction in flux was observed for the membrane casted at a thickness of 25 μm . The membranes exhibited water fluxes only at high pressure operating conditions i.e. 4 and 6 bar pressures which stabilised at 107 $\text{L.m}^{-2}.\text{hr}^{-1}$ and 171 $\text{L.m}^{-2}.\text{hr}^{-1}$ respectively. In tests for a 2 bar pressure operating condition, only a few millilitres of water passed through the membrane in the first few minutes with no further water being passed through.

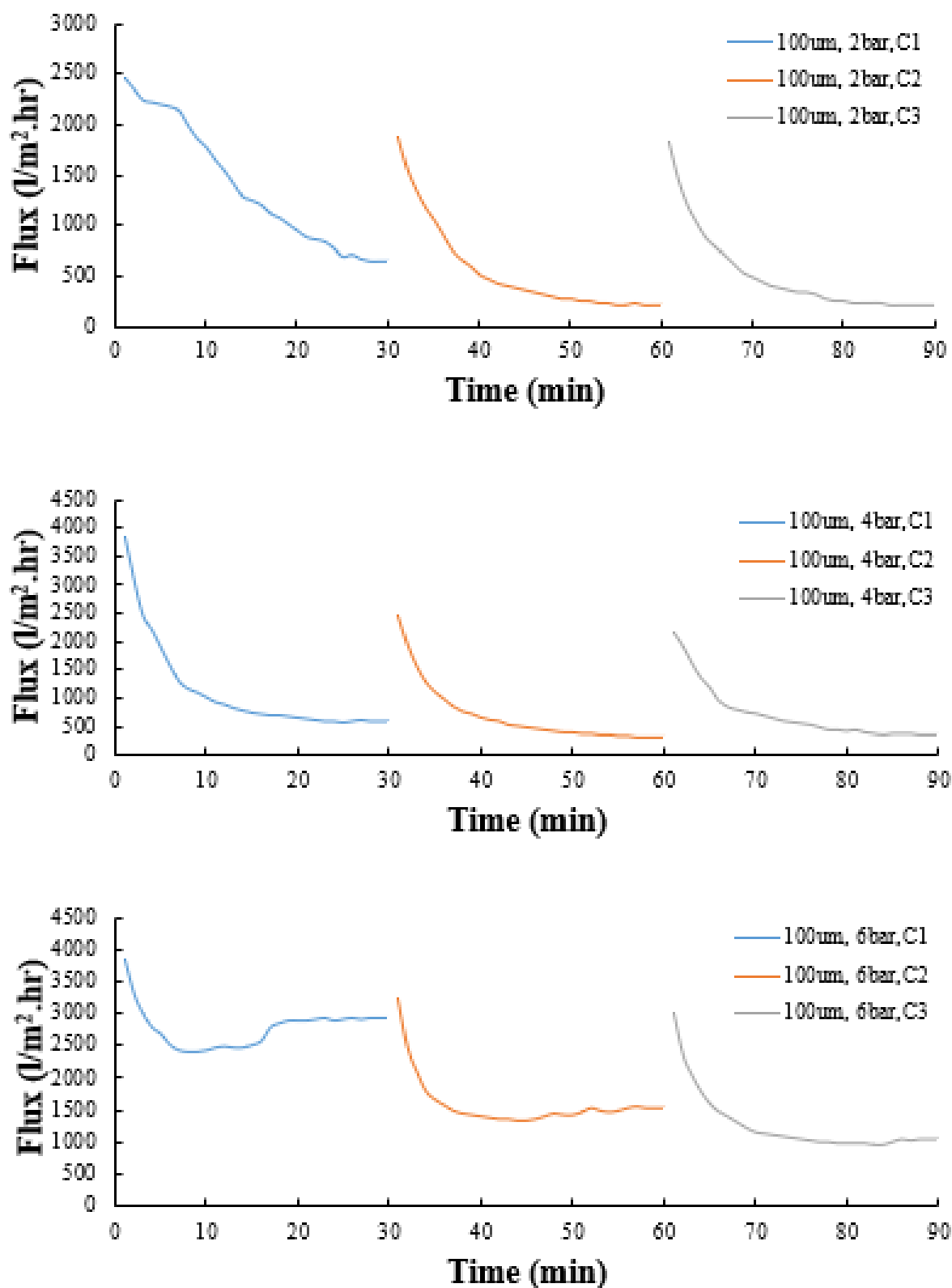


Figure 6.9: Pure water flux of PLA membranes with an initial casting thickness of 100 μ m. The membranes were operated in three cycles, each 30 minutes, under applied pressures of at 2, 4, and 6 bar.

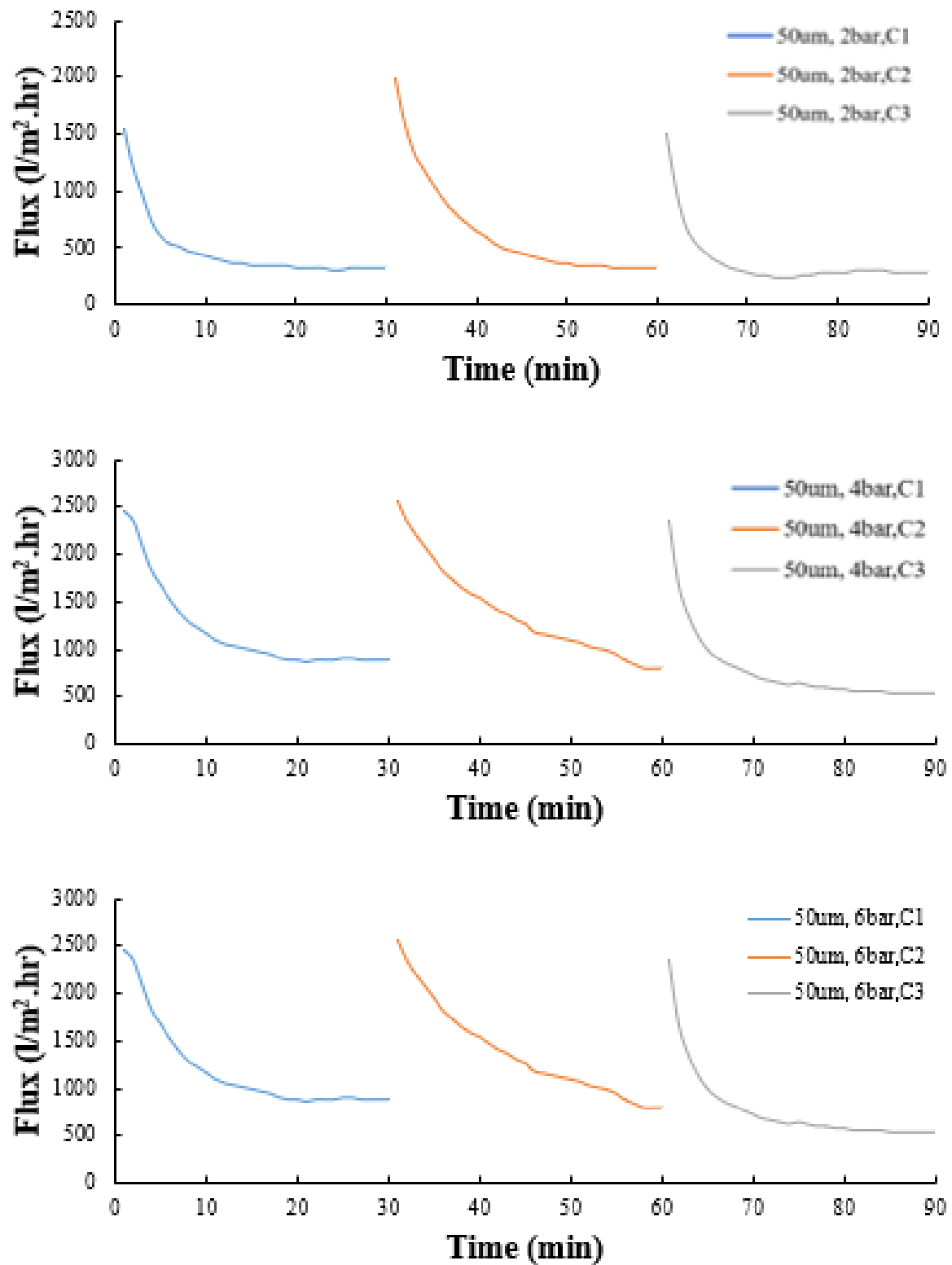


Figure 6.10: Pure water flux of PLA membranes with an initial casting thickness of 50 µm. The membranes were operated for three cycles, each 30 minutes, under applied pressures of at 2, 4 and 6 bar.

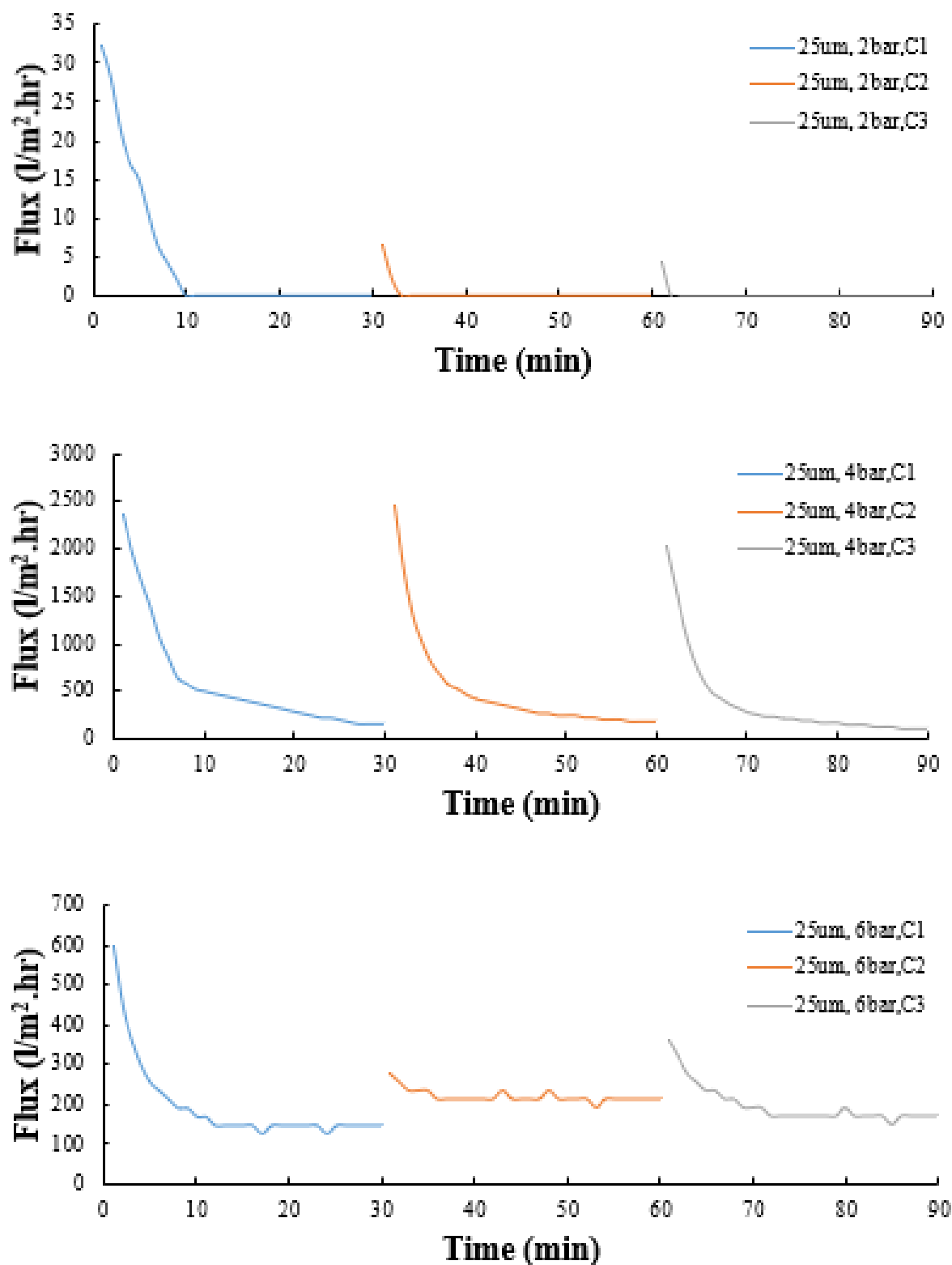


Figure 6.11: Pure water flux of PLA membranes with an initial casting thickness of 25 μm . The membranes were operated for three cycles, each 30 minutes, under applied pressures of 2, 4 and 6 bar.

The reduction in water flux with time for all the membranes regardless of their operating pressure conditions may indicate that changes in the morphology of membranes have occurred.

It can be suspected that the application of continuous pressure on the membrane lead to the collapse of some pores. To verify this, thickness measurements of membranes were conducted before and after flux tests under applied 6 bar pressure operating conditions. The reduction in thickness and porosity of PLA membranes is presented in Table 6.5 and Table 6.6 respectively. From the tabulated results in Tables 6.5 and 6.6, it can be seen that membrane thickness and porosity have reduced thus implying the collapse of some pores. Applying a pressure force on the membrane, perhaps mainly at high pressure, led to damage in the morphological structure of membranes that caused the pore to collapse thus resulting in the reduction of thickness and therefore porosity. Campbell *et al.* (2014) observed significant changes in membrane morphology with the collapse of macrovoids and a substantial decrease in thickness after testing the membrane under the application of high pressures at 6 and 27 bar pressures. Considering Tables 6.5 and 6.6, it can be understood that increasing membrane casting thickness lead to lower reduction in thickness and therefore lower loss in porosity. It is important to note that it was established and proven that water flux increases proportionally with increasing applied pressure.

Table 6.5: Membrane thicknesses before and after water flux tests under a 6 bar pressure operating condition.

Casting thickness (μm)	Thickness before testing (μm)	Thickness after testing (μm)	Reduction in thickness (%)
100	677	517	-23.6
50	293	238	-18.9
25	121	73	-39.6

Table 6.6: Membrane porosity before and after water flux tests under a 6 bar pressure operating condition.

Casting thickness (μm)	Porosity before testing (%)	Porosity after testing (%)	Reduction in porosity (%)
100	91.7	88.8	-3.2
50	90.4	88.7	-1.8
25	87.1	78.0	-10.5

The relationship between water flux and three varying operating pressure conditions for the 100µm, 50µm and 25µm thick casted membranes are shown in Figure 6.12. Ideally, the increase in flux should be proportional with applied pressure (Thomas and Corry, 2016, Haghi and Carvajal-Millan, 2014). This will lead to a characteristic membrane termed 'permeability'. Considering Figure 6.12, it can be observed that the membrane with a 50µm casting thickness exhibits an almost ideal water permeability behaviour that is characterised with a linear behaviour in relation to applied pressure ($R^2 = 0.9973$). The membrane with an initial thickness of 100µm showed non-linear behaviour with a sharp increase in flux at higher pressure, possibly as a result of damages on the surface of the membrane i.e. breakage and/or hole formations. A semi-linear behaviour with relatively low flux at a high applied pressure of 6 bar pressure was observed for the membrane cast with a thickness of 25µm. This is most likely due to the significant reduction in thickness/porosity caused by the pressure. This is emphasised further based on the results presented in Tables 6.7 and 6.8, where the 25µm thick membrane showed the highest reduction in thickness and porosity i.e. -39.6% and -10.5% respectively compared to other membranes. Therefore in terms of feasibility, it is a trade-off between increasing the operating pressure and minimising damages in the structure of the membrane to gain optimal water flux.

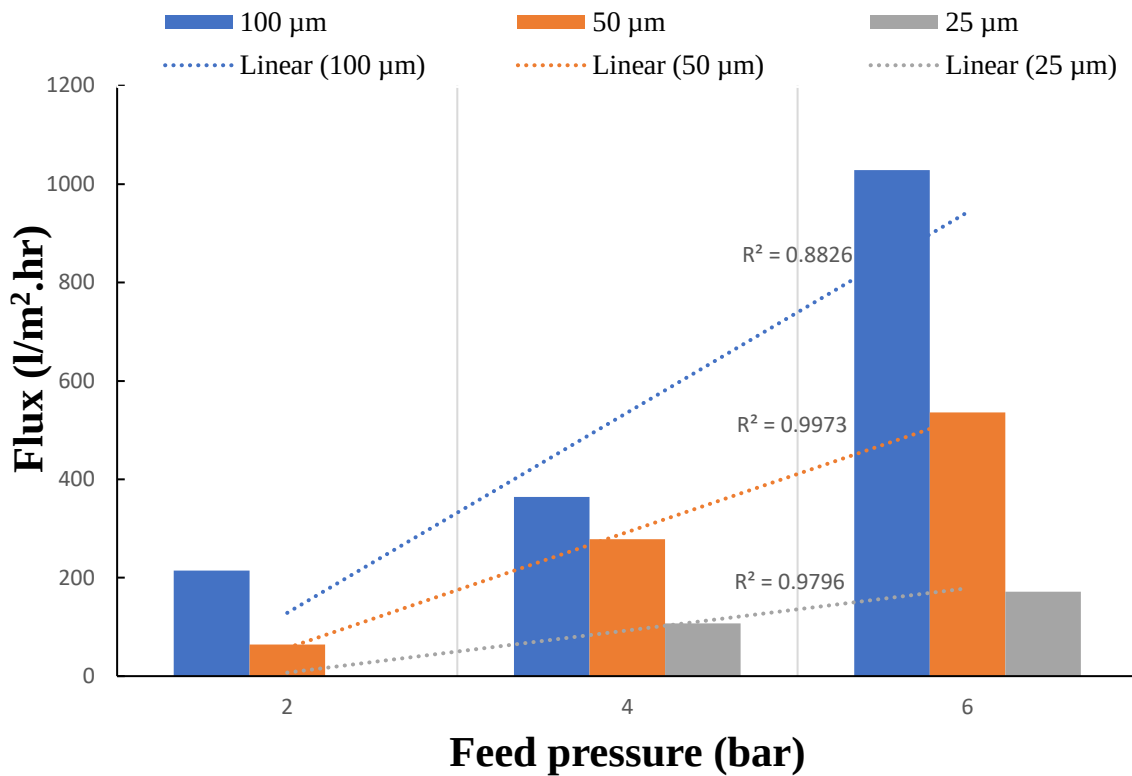


Figure 6.12: Pure water flux as function of operating pressure at varying membrane thicknesses.

The relationship between water flux and actual membrane thicknesses is graphically presented in Figure 6.13. The fluxes presented in the aforementioned figure is measured at 6 bar pressure. The fluxes were particularly considered at the operating pressure as the fluxes have more or less achieved stability. In addition, major changes in the morphological microstructure of membranes i.e. reduction in thickness have occurred before and/or at the applied 6 bar pressure. In general, pure water flux increased proportionally with increasing membrane thickness. By comparing the water flux with the actual total membrane thickness, the relationship was found to be linear with $R^2 = 0.9926$. In practical terms, the actual thickness can be considered as it would indicate effective membrane thickness for filtration. The trend of increasing water flux with increasing membrane thickness can be explained in terms of the relationship between porosity and the morphology of the microstructure. It was observed and discussed earlier in Chapter 4 (Section 4.2.2.7) that porosity increased with increasing membrane thickness. The increase in membrane porosity produces more porous channels and pathways for water to pass

through. In general, higher membrane porosity produces high water flux (Shalabya *et al.*, 2018, Gorczyca, 2018). The water flux can be controlled by the thickness of the dense layer. Even after applying a high pressure of 6 bar pressure on the fabricated membranes, the thickness and hence porosity decreased significantly as validated in Tables 6.7 and 6.8. As a consequence of the thicker dense layer(s) produced, the water flux reduced as the total membrane thickness decreased.

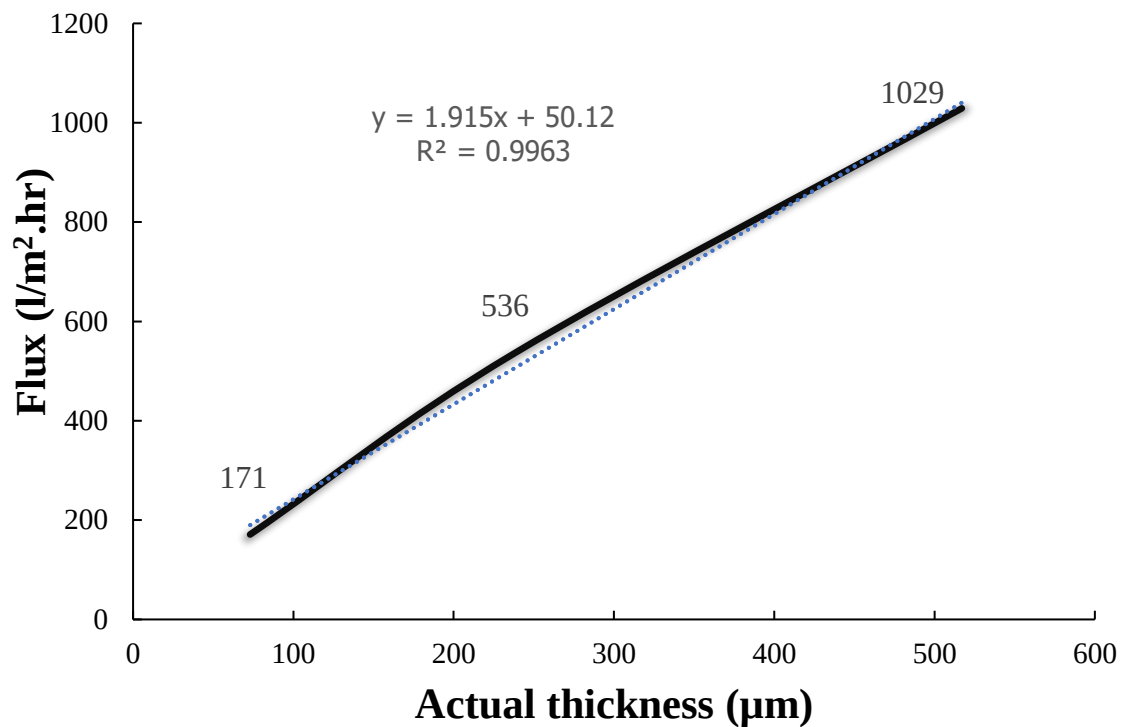


Figure 6.13: Relationship between membrane thickness and pure water flux at an applied operating pressure condition of 6 bar pressure. The actual membrane thickness was measured after the application of pressure as water flux has reached a steady state.

Changes in the morphological microstructure i.e. thickness and pore collapse was also observed by SEM as shown in Figure 6.14. From Figure 6.14, it can be seen that the membrane casted with a thickness of 100μm exhibited porous channels even after applying the 6 bar pressure thus indicating that the membrane's finger-like structural morphology has not been damaged and consequently why the water flux is the highest for this particular membrane. More or less, similar observation of undamaged porous channels was found for the film casted at 50μm. Lower flux measured in the 50μm membrane as compared to the 100 μm one, perhaps indicate

that pore size is smaller or/and the thick layer(s) is larger in the 50 μm initial thickness membrane. Unlike the membranes with initial thicknesses of 50 μm and 100 μm , the 25 μm thick membrane showed significant reduction in overall thickness and hence the occurrence of pore collapse which therefore resulted in thick layer(s) with low porosity. In addition, a non-continuous pore channel with a sponge-like-structure was exhibited before and after testing for flux which thus clarifies the reasoning for the lower flux measured in comparison to the 50 μm and 100 μm thick membranes. Emphasising the observational findings further, Campbell *et al.* (2014) examined membrane flux for several different membranes under applied pressures of 6 and 27 bar pressures. The study observed that for all tested membranes, the pores of the membrane increasingly collapsed as pressure increased which lead to denser membranes and consequently a significant decrease in flux. Studies exploring the relationship between water flux and the thickness of the dense layer found that the water flux increases as the thickness of the dense layer decreases (Niu *et al.*, 2018, Koops *et al.*, 1994, Song *et al.*, 2018, He *et al.*, 2019).

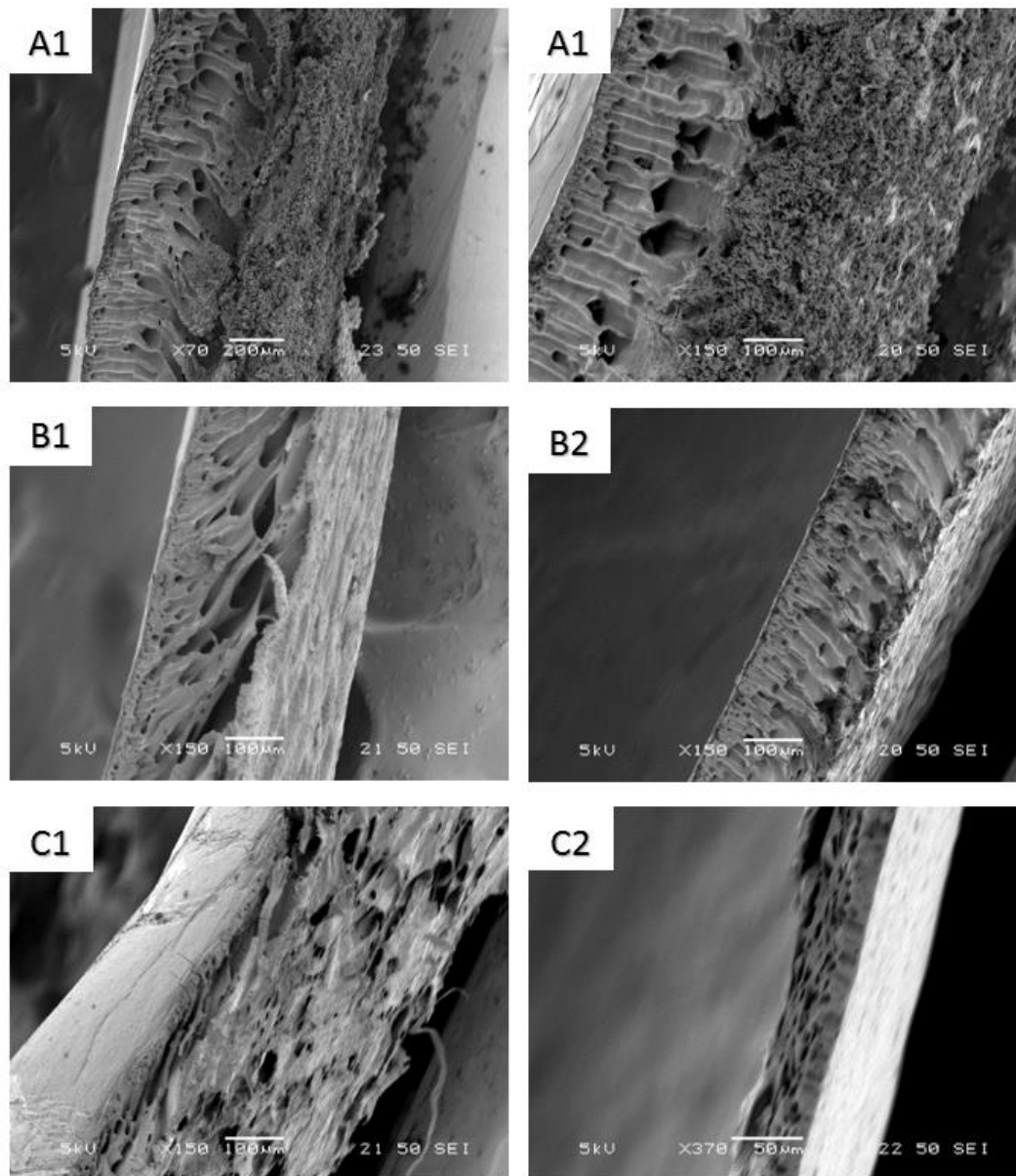


Figure 6.14: Cross-sectional SEM images of PLA membranes before and after flux testing under applied pressure of 6 bar pressure. (A1)= membrane casted at a thickness of 100µm before testing; (A2)= membrane casted at a thickness of 100µm after applied pressure for flux testing; (B1)= membrane casted at a thickness of 50µm before testing; (B2)= membrane casted at a thickness of 50µm after applied pressure for flux testing; (C1)= membrane casted at a thickness of 25µm before testing; (C2)= membrane casted at a thickness of 25µm, after applied pressure for flux testing.

The suggested relevant separation process of PLA membranes with respect to their thickness is presented in Table 6.7. Considering the table, it can be seen that PLA membranes casted at a thickness of 100µm is potentially suitable for an ultrafiltration process. Table 6.9 also shows that reducing the casting thickness leads to changes in the microstructures and different properties of the fabricated membranes. A smaller pores of membranes with a narrower and

more selective separation process was achieved as the casting thickness reduced. Membranes with an initial thickness of 50 μm demonstrates potential for use in an ultrafiltration and possibly nanofiltration processes. A characteristic nanofiltration separation process was observed for the membrane fabricated at an initial thickness of 25 μm .

The data presented earlier in Chapter 2 (Table 2.2) will be considered and compared with obtained results for measured flux in this current study to assess and determine the potential separation process for the novel fabricated PLA membranes. By analysing and comparing the results/characteristics with commercial membranes as mentioned in chapter 2, it can be implied that the membrane with a 100 μm initial thickness has an asymmetric porous microstructure with assumed pore sizes in the range of 5-200nm. An asymmetric porous microstructure with expected a relatively wide pore size range approximating between 1-200nm is characterised for the membrane casted with a thickness of 50 μm . Mulder (2012) reported that the phase inversion technique is able to produce membranes exhibiting a high porosity with a wide range of pore sizes. An asymmetric morphological microstructure with low porosity and fine pore sizes estimated between 1-5 nm is expected with the membrane cast with a thickness of 25 μm . It shall be noted here that an asymmetric porous microstructure was confirmed for all membranes via SEM as discussed in Chapter 4 (Section 4.2.2.6).

Table 6.7: Technical aspects for suggested relevant separation processes of novel PLA membranes fabricated in the current study at varying membrane thicknesses. UF: ultrafiltration and NF: nanofiltration.

Casting thickness (μm)	Flux range ($\text{L.m}^{-2}.\text{hr}^{-1}$)	Potential separation process
100	214-1029	UF
50	64-536	UF/NF
25	0-171	NF

6.4.2 Particle rejection

With experiments for pure water flux being performed, the particle rejection separation experiments were performed for the membrane with a 50 μ m initial thickness. The membrane at this particular thickness was selected because it exhibits both UF and NF filtration characteristics. In addition, the membrane also demonstrated relatively low morphological damage in consideration of the reduction in thickness and porosity under varying applied pressures. Unlike other membranes, the membrane with an initial thickness of 50 μ m exhibited more or less an ideal permeability behaviour. Red dye, milk powder, ground coffee, corn flour powder and cement were considered to examine particle rejection percentages and hence evaluate the separation performance of novel PLA membranes fabricated in this study. The separation performance of PLA/HKUST-1 MMMs after the incorporation of HKUST-1 into PLA matrix at various HKUST-1 loadings were also investigated. Particle rejection was measured after 30 minutes of continuous filtration. The percentage distribution of particle sizes of red dye, milk powder, ground coffee, corn flour powder and cement are tabulated in Chapter 3 (Table 3.3). In brief, solute rejection tests were done by preparing mixtures of solutions with a particle concentration of 0.5g/l in distilled water. The solutions were collected before filtration (feed) and after filtration (permeate) and then measured using spectrophotometry UV. The particle rejection was then calculated. More details in regards to the methodology is discussed in Chapter 3 (Section 3.5.3).

The percentage rejection after separation of various material particles via the PLA membrane cast with a thickness of 50 μ m is presented in Table 6.9. Results show a very high separation efficiency is associated with corn flour and cement with a percentage rejection of 98.5% and 97.2% respectively. Furthermore, lower particle percentage rejection was observed for milk powder and red dye at 82.6% and 72.9 % respectively. Among all tested particles, ground coffee showed the lowest separation efficiency with a percentage rejection of 65.2%.

Table 6.9: Percentage rejection for various particle types after separation via the PLA membrane with an initial thickness of 50 μ m.

Particle materials	Corn flour	Cement	Milk	Dye	Coffee
Rejection (%)	98.5	97.2	82.6	72.9	65.2

A high percentage rejection can be observed for both corn flour and cement which thus clearly demonstrates that the novel PLA membranes fabricated in this study is characterised with a high separation efficiency for the separation of selected particles. Lower percentage rejection found for other particle types i.e. milk, dye and coffee may be associated with the partial dissolution of their respective particles, perhaps the finest particles, into the water. Coffee and milk has a relatively larger particle size (mostly ranged 129 – 420 μ m) compared to corn and cement (mostly <63 μ m) as measured and tabulated in Chapter 3 (Table 3.3). Dye has the smallest particle size among all of all other particles which is also reported in Chapter 3 (Table 3.3). Milk showed separation efficiency of 82.6%, possibly due to the milk powder containing very fine particles and/or additives that could not be separated easily by a UF/NF membrane. In case of red dyes, it is most likely that some particles have not been rejected due to their fine size. Synthetic dye is usually made up of more than one component consisting of various particle sizes (Christie, 2014, Venkataraman, 2012). A high percentage rejection of synthetic dyes can be separated using NF or RO membrane processes (Sridhar, 2018, Yang *et al.*, 2019b). A low percentage rejection was observed for ground coffee most likely due to some fraction of fine coffee particles that have been fully dissolved in water. In terms of feasibility, this thus indicates that the characteristics of the membrane is not suitable in separating dissolved coffee from water. Other separation processes such as RO membrane or distillation should be considered to separate dissolved coffee from water.

The influence of the incorporation of HKUST-1 into a PLA matrix at various loadings on separation performance is graphically presented in Figure 6.15. Corn flour, red dye and coffee

particles were considered to examine the rejection efficiency. Corn flour presented the highest percentage rejection for the pure PLA membrane (0% HKUST-1 loading) with a rejection efficiency of 98.5%. The addition of HKUST-1 into PLA matrix led to a reduction in rejection efficiency. Compared to the pure PLA membranes, the rejection efficiency decreased by 6%, 9.5% and 7.6% at HKUST-1 loadings of 5wt%, 10wt% and 20wt% respectively. The rejection efficiency decreased as HKUST-1 loading increased to 10wt% before it started to increase again. A similar trend can be observed for red dye particles. The highest rejection efficiency for red dye was achieved at 20wt% HKUST-1 loading with a rejection efficiency of 73.4%. This was followed by pure PLA and then the membrane at 10wt% HKUST-1 loading with rejection efficiencies of 72.9% and 61.7% respectively. It is important to note that the rejection efficiency of the 5wt% HKUST-1 loaded membrane could not be measured using the UV instrument and therefore no data has been reported in regards to this. A reduction in particle rejection efficiency with increasing HKUST-1 loading was observed for ground coffee particles. The pure PLA membrane exhibited a particle rejection efficiency of 65.2% which gradually reduced to 62.1%, 54.1% and 34.2% as HKUST-1 was incorporated at 5wt%, 10wt% and 20wt% loading, respectively.

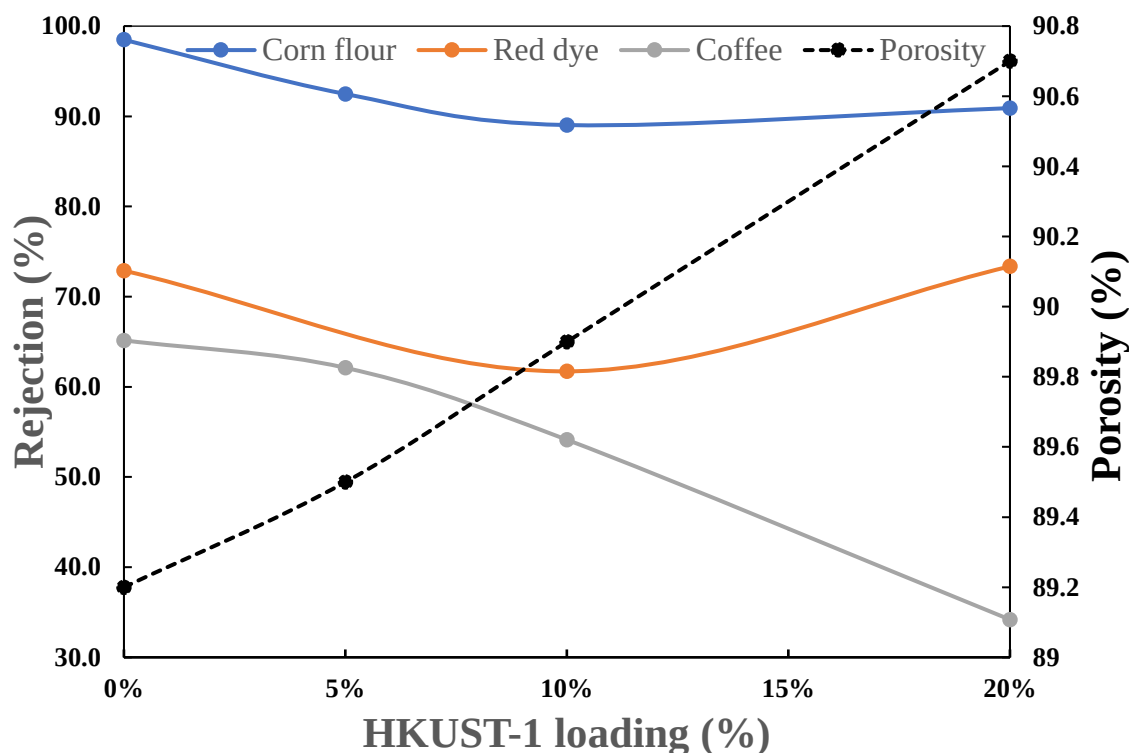


Figure 6.15: Percentage rejection for the separation of selected particle types via PLA/HKUST-1 membranes in tandem to porosity at various HKUST-1 loadings.

By combining and comparing all three results for particle rejection, it can be clearly observed that there is no general trend in the rejection efficiency of all particles as HKUST-1 loading increased. This is likely due to either the structure of the membranes and/or the characteristics of the particles. The incorporation of different HKUST-1 loadings lead to changes in the properties and morphology of the polymer phase of resulting membranes i.e. porosity/tortuosity of the selective and support layers. Lower rejection efficiencies may indicate that the membrane exhibited high macrovoids and porosity as a result of poor adherence between the HKUST-1 and PLA. In agreement to this, results discussed in Chapter 5 (Section 5.2.5) demonstrated that HKUST-1 loading proportionally increased the porosity of membranes. The influence of incorporated HKUST-1 loading on porosity is shown in Figure 6.15. The incorporation of HKUST-1 loading into PLA matrix has increased the porosity to 89.5%, 89.9%, and 90.7% for 5wt%, 10wt% and 20wt% HKUST-1 loaded PLA/HKUST-1 MMMs respectively compared to a porosity of 89.2% for pure PLA membrane. The other

possible reason of the increases in the membrane porosity as HKUST-1 loading increased could be related to the characteristics i.e. particle size/distribution of selected particles (corn flour, red dye and grinded coffee). HKUST-1 is a porous material and therefore some of those particles, or a partial fraction of each one, have passed through the pores of HKUST-1 and consequently enhanced the selectivity of the membrane for some selected particles. This thus implies that increasing the loading of HKUST-1 is a trade-off between membrane porosity and membrane selectivity/rejection efficiency thus believably influences the membrane permeability/flux.

Similar to observations found in the current study, Campbell *et al.* (2016) investigated polystyrene particle rejection efficiency in consideration of polyimide/HKUST-1 MMMs at various HKUST-1 loadings. Results showed no general trends between the loading of HKUST-1 and rejection efficiency. The study also found that HKUST-1 loading has no effect on the selective layer of fabricated membranes. Moriya *et al.* (2009) investigated the influence of incorporating 5wt, 10wt and 20wt% loadings of PEG particles into hollow PLA fibre membranes. In the BSA rejection experiment, the aforementioned study found that the percentage rejection was approximately 80% for pure PLA membranes and at the 5wt% as well as 10wt% PEG loaded membranes. However, their results showed that increasing PEG loading to 15wt% led to a significant increase in water permeability in addition to a major reduction in BSA rejection from about 80% of pure PLA membrane to 55.8%. The influence of the addition of different PEG loadings on the mechanical property defined in terms of tensile stress was also examined in the study. They observed that increasing PEG loading resulted in the decrease of tensile stress. Results presented in this chapter (Section 6.2.1) are in agreement to the results from Moriya *et al.* (2009) whereby the mechanical properties i.e. tensile strength reduced as HKUST-1 loading increased. Based on the results for particle rejection, it can therefore be

implied that the membrane separation processes for MF, UF or NF can be considered and obtained by controlling HKUST-1 loading into the PLA matrix membrane.

6.5 Summary

Membrane durability and performance have been explored and discussed in this chapter. The mechanical properties of pure PLA membranes and PLA/HKUST-1 MMMs fabricated at initial thicknesses of 25 μ m, 50 μ m, and 100 μ m and immersed in a 25°C water bath for 10 minutes, 90 minutes and 24 hours were examined. Results obtained from mechanical testing showed no generalised trend. No significant difference was determined in changing the initial thickness and not the immersion time for both pure PLA membranes and PLA/HKUST-1 MMMs. In addition, the selected fabrication conditions (50 μ m initial casting thickness and immersion in a 25°C water bath for 90 minutes) were considered to examine the mechanical properties of PLA/HKUST-1 MMMs at 5wt, 10wt, 20wt% HKUST-1 loadings. A significant reduction in mechanical properties was observed as the loading of HKUST-1 incorporated into the PLA matrix increased due to the poor/ non-uniform distribution of HKUST-1 particles into PLA matrix.

A degradation study was conducted using a pure PLA membrane prepared at an initial casting thickness of 50 μ m and immersed in a 25°C water bath for 90 minutes. Due to the long degradation time of PLA in atmospheric conditions, an accelerated degradation study was considered by immersing the PLA membrane in a hot water bath at 50°C. Results demonstrated that the PLA membranes were capable of remaining mechanically stable up to 77 days before any substantial mechanical damage or mass loss occurs. Considering its equivalency to room temperature conditions, 25°C, the novel PLA membranes fabricated in this study are expected to survive for more than two years before any significant damage or mass loss.

Experiments for pure water flux were conducted at 2, 4 and 6 bar pressures for pure PLA membranes fabricated with initial casting thicknesses of 25 μ m, 50 μ m and 100 μ m to assess the influence of membrane thickness in relation to the applied pressure on water flux performance. Results demonstrated that the application of higher pressure led to higher water flux and hence permeability but at the cost of more damage to the membrane's morphological structure. Membrane thickness was found to have a direct relationship with water flux wherein membrane thickness increased membrane porosity and hence increased water flux in a proportional manner. Furthermore, it was found that the membrane fabricated with a 25 μ m initial casting thickness exhibited the water flux characteristics of nanofiltration separation processes while features for an ultrafiltration separation process was observed for the membrane with a 100 μ m initial thickness. The membrane with a 50 μ m initial thickness was determined to have the potential to be used in both ultrafiltration and nanofiltration separation processes.

The separation performance was examined for selected pure PLA membrane and PLA/HKUST-1 MMMs. The membrane with a 50 μ m initial membrane thickness was considered to examine the rejection efficiency of the pure PLA membrane. The pure PLA membrane has successfully separated several material particles with a high rejection efficiency of 98.5% and 97.2% being observed for corn flour and cement particles respectively. The same membrane fabrication conditions (50 μ m initial casting thickness and immersion in a 25°C water bath for 90 minutes) was considered to examine the rejection efficiency for selected material particles of PLA/HKUST-1 MMMs at varying HKUST-1 loading. Results showed that the rejection efficiency enhanced for some particles at high HKUST-1 loadings and reduced for other particle types. Incorporation of HKUST-1 into PLA matrix at varying HKUST-1 loading led to changes in the microstructures of PLA/HKUST-1 MMMs. It was found that altering the loadings of HKUST-1 is a trade-off between membrane porosity and

Chapter 6: Evaluation of membranes performance and durability

membrane filtration performance i.e. rejection efficiency because as the porosity of membrane increased the rejection efficiency reduced and vice versa.

Chapter 7: Conclusions and future work

7.1 Conclusions

The focus of this study was the fabrication, characterisation and evaluation of pure PLA membranes as well as composite PLA/MOFs mixed matrix membranes. Pure PLA and composite PLA/MOFs membranes have been reported to be used in sectors involving gas separation, but have not yet been widely investigated in applications involving liquid separation i.e. water membranes. The reason for investigating these membranes was to manufacture sustainable membranes that exhibit high water flux, high solute rejection and characterised with excellent thermal/mechanical/chemical stabilities. The novelty of this study lies in the manufacturing of porous flat PLA sheets and PLA/MOFs membranes through the use of a commercial phase inversion via immersion precipitation technique which to the best current knowledge has not been addressed.

PLA biopolymers were chosen in this study for the fabrication of novel porous flat PLA membrane sheets through the phase inversion via immersion precipitation technique casted at a thickness of 150 μ m. The influence of treating PLA pellets prior to use in the fabrication of the membranes was investigated. Furthermore, the influence of the type of non-solvent, PLA concentration and drying method were all also explored and discussed. Observational results from SEM imaging showed that the fabricated membranes exhibited asymmetric skinned porous structures with patterns of dense top layer supported by a bottom porous layer. In addition, TGA and DSC analysis demonstrated that membranes prepared from untreated PLA pellets exhibited higher thermal stability and thermal properties compared to membranes prepared from pre-treated pellets (dried and melted pellets). Considering the type of non-solvent used for the immersion bath, membranes immersed in water as the non-solvent showed higher thermal stability and thermal properties compared to membranes immersed in

50/50 v/v% water/methanol. Regarding investigations looking into the influence of PLA concentration, it was found that the membrane fabricated at a PLA concentration of 10% offered the most optimum morphological surface structure while also exhibiting the highest thermal stability and thermal properties compared to other membranes fabricated at other different PLA concentrations. In regards to the drying method, it was observed that implementing a vacuum oven for further drying after subsequent initial drying using a conventional oven set at 40°C for 24 hours led to collapse and damage in the structure of the membrane. Implementing only the conventional oven on the other hand gave flat continuous membranes with no damage in the structure. The influence of changing the casting thickness was also investigated due to shrinkage that was observed for some membranes. Results showed significant improvements in the surface morphology as the casting thickness was decreased. Thus caused as a result of the quick film formation because of the rapid phase exchange, diffusion, between the solvent and the non-solvent. The investigation determined that the most optimum membrane was cast at a thickness of 50µm. The aforementioned membrane was fabricated with a unique continuous morphological surface structure without any shrinkage or brittleness.

PLA-MOFs MMMs were fabricated using the established preparatory conditions for the fabrication of pure PLA membranes. HKUST-1 and MIL-53 MOFs with 5wt% loading were incorporated into a PLA matrix to produce porous flat PLA/HKUST-1 and PLA/MIL-53 MMMs sheets. The MOFs were successfully incorporated into the PLA matrix membranes which was confirmed via XRD. In addition, SEM imaging demonstrated that the novel fabricated PLA/MOFs MMMs exhibited an asymmetric skinned porous structure. For further and detailed investigations into MMMs, HKUST-1 MOF was considered and explored in this study. The influence of changing casting thickness, the immersion time and immersion temperature of PLA/HKUST-1 MMMs were investigated. Similar for pure PLA membranes,

the PLA/HKUST-1 membrane fabricated with a thickness of 50 μ m exhibited the most continuous morphological surface structure with no shrinkages and brittleness. The PLA/HKUST-1 membrane immersed in a 25°C water bath for 90 minutes also exhibited the most optimum morphological structure and exhibited fairly superior thermal stability and thermal properties. It is also important to note that the aforementioned membrane incorporated the appropriate amount of MOF. The effect of increasing HKUST-1 loading into the PLA/HKUST-1 matrix was also explored at HKUST-1 loadings between 5-40wt%. PLA/HKUST-1 MMMs were successfully produced at HKUST-1 loadings of 5wt%, 10wt% and 20wt%. However, membranes fabricated at HKUST-1 loadings of 30wt% and 40wt% did not form due to bad interaction which caused big voids between the HKUST-1 particles and PLA chains. Considering the successfully formed PLA/HKUST-1 MMMs, increase in HKUST-1 loading increased the amount of HKUST-1 incorporated into PLA/HKUST-1 as was evident and confirmed from XRD analysis. Based on DSC analysis, no remarkable changes in terms of thermal properties was found as the HKUST-1 loading increased. Huge and systematic reductions in thermal stability and weight loss was evident from TGA analysis as the HKUST-1 loading increased. In consequence of increasing HKUST-1 loading, the morphology of the membranes became increasingly weaker and brittle due to the poor adherence between the HKUST-1 particles and PLA biopolymer chains. The resulting morphology of the membranes were physically detectable and was proven via mechanical testing.

The durability of membranes were examined by investigating the degradation of fabricated PLA membranes in addition to testing and comparing the mechanical strength of pure PLA and PLA/HKUST-1 membranes. Degradation studies verified that the novel fabricated PLA membranes fabricated in this study is capable of surviving for more than two months in hot water at a temperature of 50°C, before any significant adverse effects on its structure and mechanical strength occurs. From this study, it is estimated that the novel fabricated

membranes are able to survive and operate for approximately two years at 25°C under practical operational conditions.

From studies in regards to mechanical strength, it was determined that pure PLA membranes exhibited higher mechanical strength compared to PLA/HKUST-1 MMMs regardless of their initial casting thickness because of the weak adherence between the PLA and HKUST-1 particles. Pure PLA and PLA/HKUST-1 membranes exhibited failure in the range of approximately ~1-1.5MPa and ~0.5-1MPa respectively. Adding to the above, it was observed that the mechanical strength reduced as HKUST-1 loading increased and consequently the membranes became more brittle as a consequence of some voids that caused via the bad interfacial interaction between the HKUST-1 particles and PLA chains.

Pure water flux and particle rejection tests were performed to evaluate the filtration performance of the fabricated membranes. Pure water flux tests were conducted for pure PLA membranes cast at initial thicknesses of 25µm, 50µm and 100µm at elevated pressures of 2, 4 and 6 bar. Results show that water flux increased proportionally with the increase in applied pressure regardless of their initial membrane thickness. However, the morphological structure of the membranes were found to be increasingly damaged as a result of pores collapse. Pure water flux was determined to increase with increasing membrane thickness because of the proportional increase in the porosity as the membrane thickness was increased. In the context of commercial membrane separation features, PLA membranes fabricated with initial thicknesses of 25µm, 50µm and 100µm exhibited water fluxes characteristic of NF, UF/NF and UF, respectively.

Particle rejection was examined for selected pure PLA membranes and PLA/HKUST-1 MMMs to evaluate separation performance. Pure PLA membranes successfully separated several different types of micro-sized particles at a high rejection efficiency of +97%. Particular types

of particles were considered in evaluating the separation performance of PLA/HKUST-1 MMMs with HKUST-1 loadings of 5wt%, 10wt% and 20wt%. Regardless of particle type, no general trend was observed in the efficiency of particle rejection as HKUST-1 loading was increased. Considering the microstructure of membranes, membranes with higher porosity gives lower particles rejection but higher water flux. It is therefore implied that changing and choosing the appropriate HKUST-1 loading is a trade-off between the characteristics of the membrane's structure i.e. porosity, and the filtration performance of the membrane i.e. rejection efficiency/selectivity.

7.2 Recommendations for future work

The functional group chemistry and structure of MOFs highly influences the properties and characteristics i.e. membrane stability and selectivity of the final fabricated membrane. It could therefore be of crucial benefit to examine different types of MOFs, especially those that are more stable in water i.e. UiO-66 and UiO-67.

In this study, the conventional fabrication mechanism of PLA/MOFs MMMs have been explored. In order to improve the adherence between the MOF and PLA in addition to enhancing membrane properties and subsequently filtration properties, alternative fabrication mechanisms can be addressed. For example, exploring the mechanism of in-situ growth (ISG) membranes whereby MOFs are grown inside the pre-existing pores of the polymeric membrane.

This study has established a scope in terms of controlling fabrication parameters to improve the overall properties and characteristics of membranes. For instance, the morphological structure of membranes can be modified by controlling and optimising the thickness of membranes. A uniform surface structure exhibiting uniform pore size and distribution was able to be obtained as a result. Investigations in terms of technique which allow possible adjustments

of such parameters for example can be performed. Such techniques such as spin coating is a very useful fabrication technique that can be used to optimise the desired features of membranes by tuning spinning parameters i.e. spinning speed and time.

At this stage, it is recommended that more effort is put on this area of research to understand and determine if bio-polymeric based membranes can be applied in realistic contexts of liquid membrane applications. Designing and manufacturing membranes with larger surface areas and examining them under actual industrial operational conditions could be very useful to evaluate the performance of aforementioned membranes for the benefit of realistic industrial applications. Finally, the potential use of these membranes in different liquid membrane applications such as in the petroleum industry i.e. oil/water separation, and the medical field i.e. haemodialysis should be explored.

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Appendices

A

The morphologies of PLA films prepared casted at 50 μm and immersed in 25 $^{\circ}\text{C}$ water bath for 24 hours and 90 minutes are shown in Figure A.1. Both films showed a similar pattern of asymmetric membranes microstructure. Top dense layer supported with porous bottom layer, with finger-like structure were formed for both films. According to the SEM images, no difference in the microstructural morphology was spotted for both films.

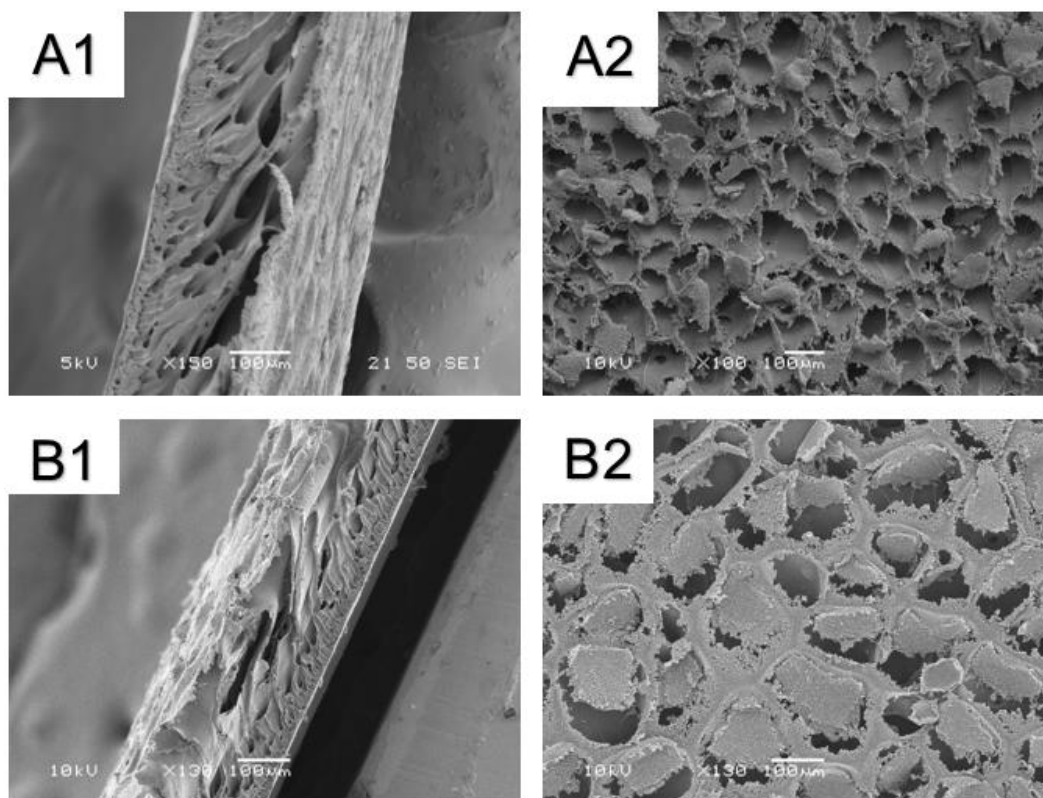


Figure A.1; Cross-sectional and top view of the SEM images of PLA films casted at 50 μm thicknesses, then immersed in 25 $^{\circ}\text{C}$ water bath for 90 minutes and 24hours. (A1&A2)= film immersed for 24hours. (B1&B2)= film immersed for 90 minutes.

Crystal structures for both PLA films casted at 50 μm and immersed in 25 $^{\circ}\text{C}$ water bath for 24 hours and 90 minutes are shown in Figure A.2. Both films exhibited almost identical crystal structure with a pattern of the amorphous structure, as both films displayed large wide peak

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with no sharp peak-characteristic of an amorphous structure. What is more, DSC results confirmed that both films resulted nearly equal crystallinity. This perhaps tells that immersing PLA films for various immersion time has not changed the film's crystal structure and crystallinity.

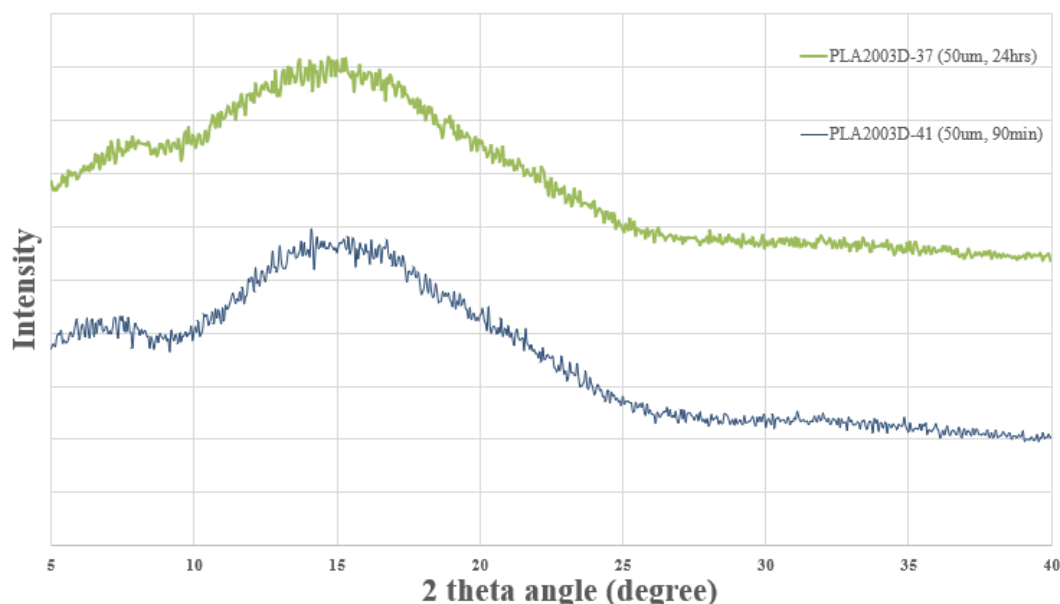


Figure A.2; XRD data for PLA films crystals from 5° to 40° that casted at 50μm thicknesses, then immersed in 25°C water bath for 90 minutes and 24hours. PLA2003D-37= film immersed for 24hours. PLA2003D-41= film immersed for 90 minutes.

Thermal properties of PLA films cast at 50 μm and immersed in a 25 °C water bath for 24 hours and 90 minutes are shown in Table A.1. DSC results showed that an increase in the T_g from 59.7 °C by 1 °C was observed after the film immersed for the shorter time (90minutes). The increase in the T_g has consequently shifted up the T_c value from 95.3 °C to 97.0 °C for the film immersed for 90 minutes. The increase in the T_g possibly indicates that the film immersed in the shorter time has less chains mobility. In addition, both melting temperature and crystallinity nearly remains similar for both films.

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Table A.1: Thermal properties of the PLA films casted at 50µm thicknesses, then immersed in 25oC water bath for 90 minutes and 24hours. PLA2003D-37= film immersed for 24hours. PLA2003D-41= film immersed for 90 minutes. (First heating).

	T_g (°C)	T_c (°C)	T_m (°C)	χ_{DSC} (%)
PLA2003D-37 (24hours)	59.7	95.3	155.8	8.1
PLA2003D-41 (90minutes)	60.7	97.0	155.5	8.0

Film stability was studied by TGA for both PLA films cast at 50 µm and immersed in a 25 °C water bath for 24 hours and 90 minutes. Table A.2 shows that film immersed for 90 minutes showed slight reduction in the 5 and 50% thermal stabilities by 4 °C as compared to the film immersed for 24 hours. In addition, weight losses were comparably equal for both films as shown in Table 6A.2 and Table A.3. The difference in the thermal stability can be neglected because it is only 4 °C, which even did not influence the weight loss values. Besides, weight loss values indicate that both films were fully dried and do not contains DMSO residue.

Table A.2: TGA results of the PLA films casted at 50µm thicknesses, then immersed in 25oC water bath for 90 minutes and 24hours. PLA2003D-37= film immersed for 24hours. PLA2003D-41= film immersed for 90 minutes.

	Thermal stability at 5% (°C)	T_d (°C)	Residue at 600 °C (%)
PLA2003D-37 (24hours)	314	361	0.42
PLA2003D-41 (90minutes)	310	357	0.41

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Table A.3: A comparison of weight loss at 100 and 189 °C, for the PLA films casted at 50µm thicknesses, then immersed in 25oC water bath for 90 minutes and 24hours. PLA2003D-37= film immersed for 24hours. PLA2003D-41= film immersed for 90 minutes.

	Weight Loss at 100 °C	Weight Loss at 189 °C
	(%)	(%)
PLA2003D-37 (24hours)	0.35	0.36
PLA2003D-41 (90minutes)	0.33	0.33

B

Below tables summarise the stabilised fluxes for two measurements methods. Method one: is to apply a pressure in a sequence/order of 2, 2, 2; 4, 4, 4; 6, 6, 6 bar. Method two: is to apply a pressure in a sequence/order of 2, 4, 6; 2, 4, 6; 2, 4, 6 bar. In summary, method one showed more water fluxes besides more stabilised flux at various applied pressures. In addition, method one resulted less reduction in the thickness and porosity, indicating lower morphological damages i.e., pores collapses as compared to method two. Therefore, method one was considered to perform the pure water flux test and evaluate the filtration performance for our fabricated membranes.

Pure water flux results

Measurements Method one: 2, 2, 2; 4, 4, 4; 6, 6, 6 bar.

For: 100µm membrane

Table B.1: Pure water flux for the membrane with 100µm thickness. Test run in the order of 2,2,2; 4,4,4; 6,6,6 bar.

Operating Pressure (bar)	Flux1 (l/m ² .hr)	Flux2 (l/m ² .hr)	Flux3 (l/m ² .hr)
2	643	214	214
4	579	321	364
6	2936	1543	1029

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For: 50µm membrane

Table B.2: Pure water flux for the membrane with 50µm thickness. Test run in the order of 2,2,2; 4,4,4; 6,6,6 bar.

Operating Pressure (bar)	Flux1 (l/m ² .hr)	Flux2 (l/m ² .hr)	Flux3 (l/m ² .hr)
2	107	86	64
4	321	321	279
6	879	793	536

For: 25µm membrane

Table B.3: Pure water flux for the membrane with 25µm thickness. Test run in the order of 2,2,2; 4,4,4; 6,6,6 bar.

Operating Pressure (bar)	Flux1 (l/m ² .hr)	Flux2 (l/m ² .hr)	Flux3 (l/m ² .hr)
2	0	0	0
4	150	193	107
6	150	214	171

Measurements Method two: 2, 4, 6; 2, 4, 6; 2, 4, 6 bar.

For: 100µm membrane

Table B.4: Pure water flux for the membrane with 100µm thickness. Test run in the order of 2,4,6; 2,4,6; 2,4,6 bar.

Operating Pressure (bar)	Flux1 (l/m ² .hr)	Flux2 (l/m ² .hr)	Flux3 (l/m ² .hr)
2	54	75	43
4	150	161	75
6	386	343	171

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For: 50µm membrane

Table B.5; Pure water flux for the membrane with 50µm thickness. Test run in the order of 2,4,6; 2,4,6; 2,4,6 bar.

Operating Pressure (bar)	Flux1 (l/m ² .hr)	Flux2 (l/m ² .hr)	Flux3 (l/m ² .hr)
2	86	43	28
4	182	64	39
6	171	86	64

For: 25µm membrane

Table B.6 Pure water flux for the membrane with 25µm thickness. Test run in the order of 2,4,6; 2,4,6; 2,4,6 bar.

Operating Pressure (bar)	Flux1 (l/m ² .hr)	Flux2 (l/m ² .hr)	Flux3 (l/m ² .hr)
2	2	0	0
4	75	21	32
6	75	75	64

Reduction % in film thickness after flux took place at 6 bar

Measurements Method one: 2, 2, 2; 4, 4, 4; 6, 6, 6 bar.

Table B.7 Reduction % in film thickness after water flux took place at 6 bar at varying thicknesses. Test run in the order of 2,2,2; 4,4,4; 6,6,6 bar.

Initial casting thickness (µm)	Reduction in thickness (%)	Reduction in porosity (%)
100	-20.8	-3.2
50	-25.6	-6.3
25	-37.5	-19.5

Measurements Method two: 2, 4, 6; 2, 4, 6; 2, 4, 6 bar.

Table B.8 Reduction % in film thickness after water flux took place at 6 bar at varying thicknesses. Test run in the order of 2,4,6; 2,4,6; 2,4,6 bar.

C	Initial casting thickness	Reduction in thickness	Reduction in porosity
	(μm)	(%)	(%)
	100	-16.8	-3.3
	50	-29.3	-7.8
	25	-45.5	-22.0

The figures on the following pages (Figure C.1 to C.5) present the particles size distributions of milk powder, ground coffee, corn flour, cement and red dye. Table C.1 summarises the particles size distributions.

Table C.1; The particles size distributions of milk powder, ground coffee, corn flour, cement and red dye.

Mesh size (μm)	Particles weight distributions (%)				
	Milk powder	Coffee	Corn flour	Cement	Red dye
63<	0	0	86.7	78.7	100 ($1.5\mu\text{m}<$)
63-125	3.4	3.6	0.5	14.8	0
125-149	3.4	2.6	0.1	0.2	0
149-177	12.6	16.4	11.7	3.7	0
177-250	46.8	14.8	0.2	0.3	0
250-420	26.3	54.5	0.1	0.2	0
>420	7.4	8.2	0.6	2.2	0

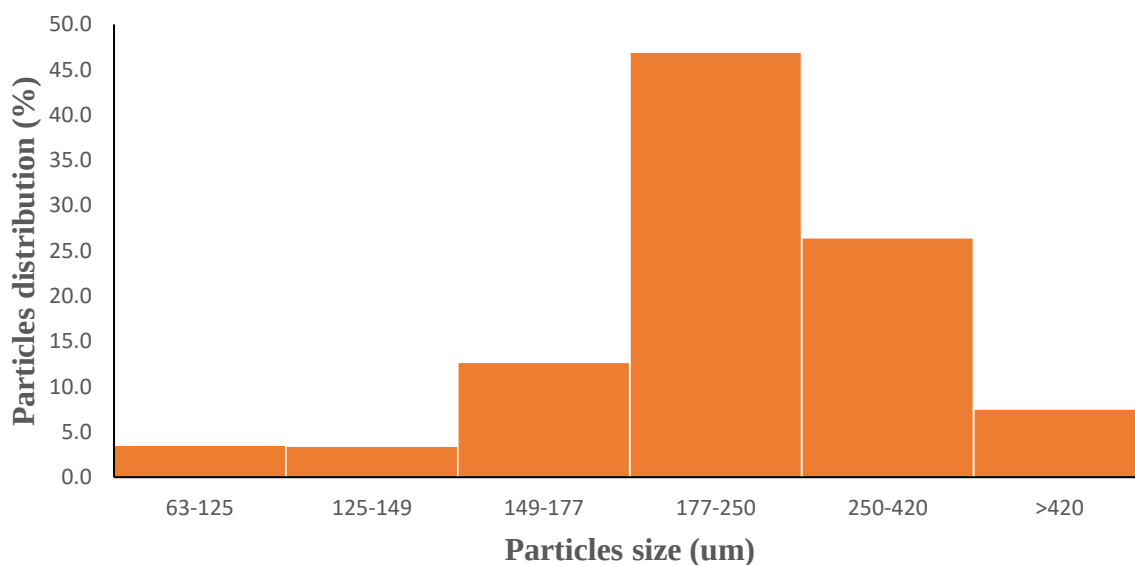


Figure C.1; The particles size distributions of milk powder.

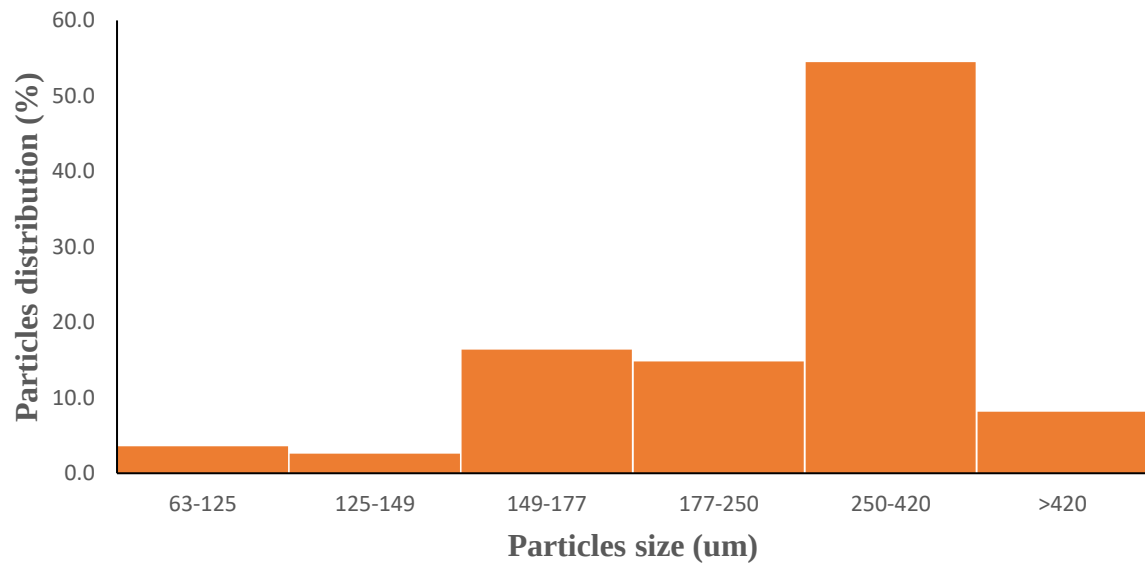


Figure C.2; The particles size distributions of coffee grounded.

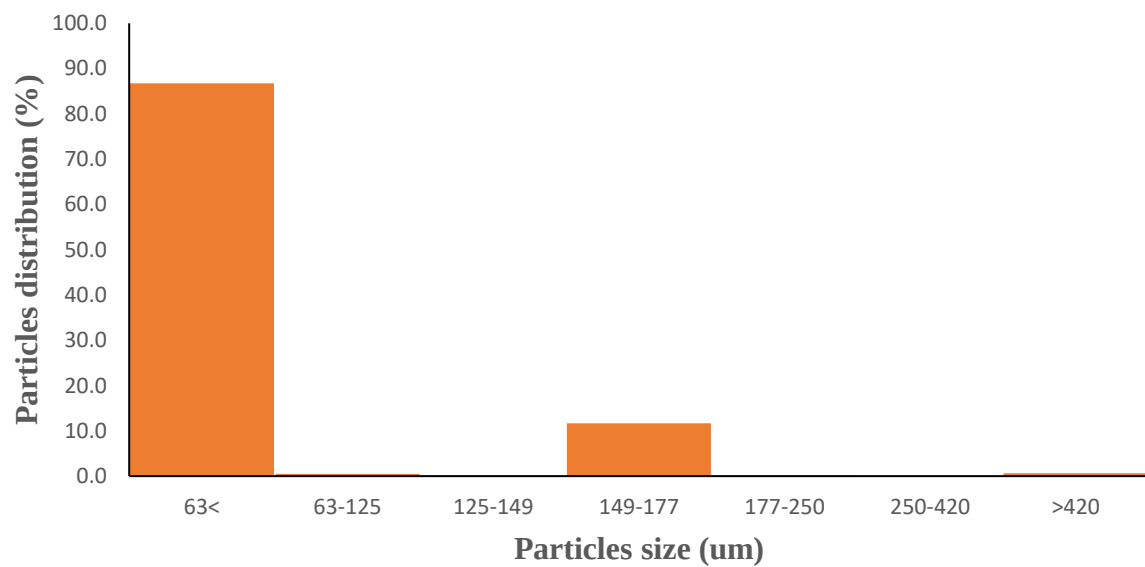


Figure C.3; The particles size distributions of corn flour.

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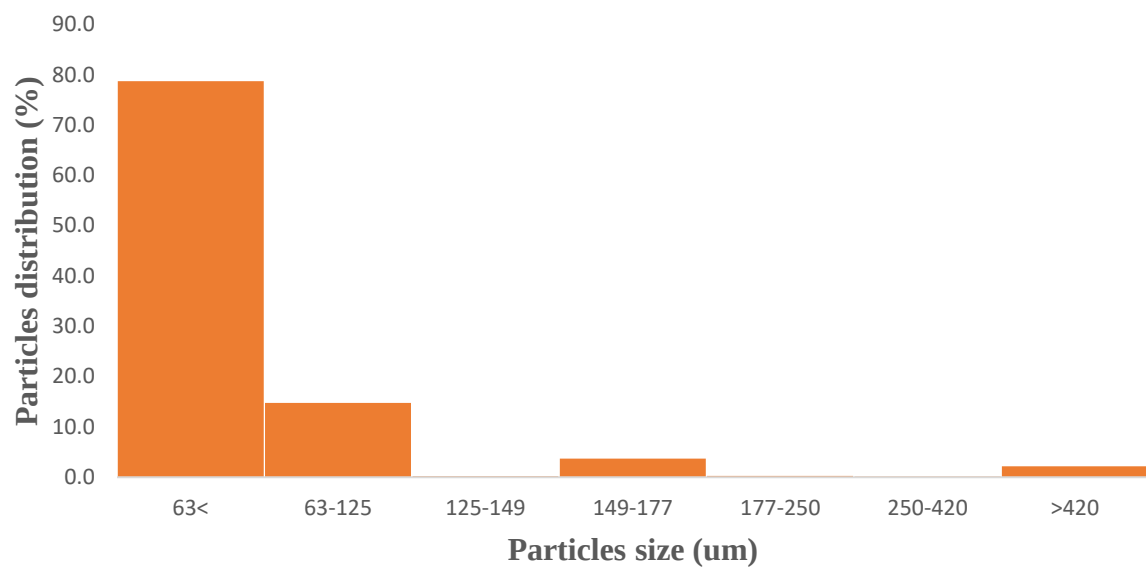


Figure C.4; The particles size distributions of cement.

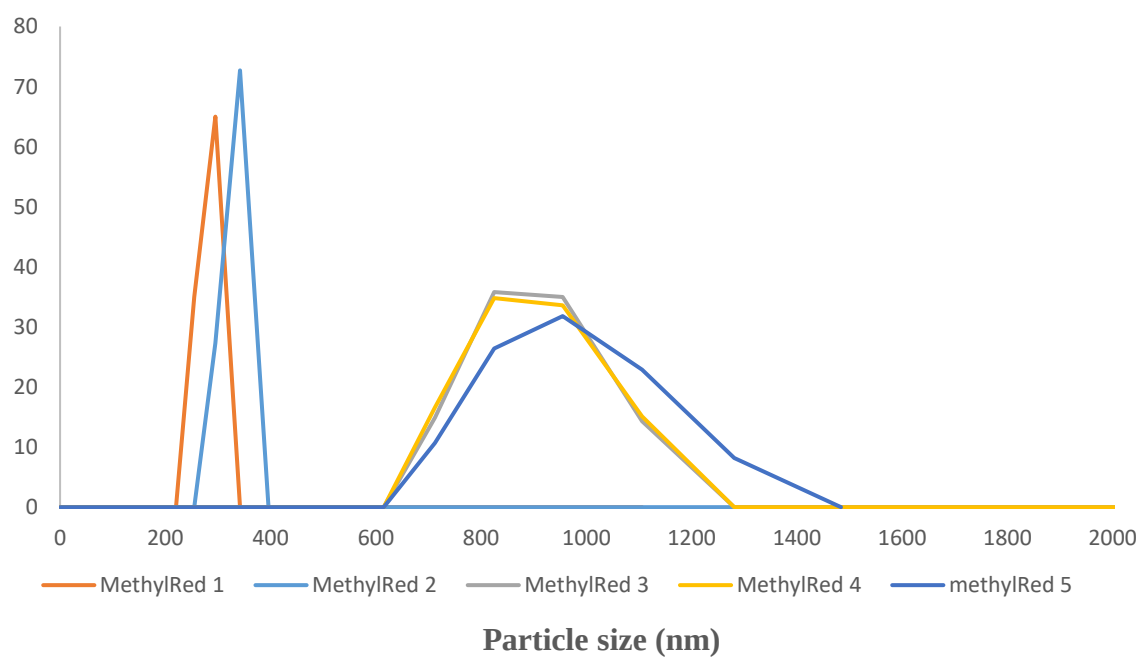


Figure C.5; The particles size distributions of methyl red dye.