

Development of a robust throughput process for the production of PMMA membranes via a TIPS–air casting method



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Declaration

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Niall Murphy

Abstract

Development of a robust throughput process for the production of PMMA membranes via a TIPS–air casting method

Niall Murphy

Lateral flow membranes (membranes that allow movement of fluid across the membrane rather than through it) play a crucial role in the functionality of immunoassay devices determining performance speed and assay reliability. These devices are increasingly important, being used for an expanding range of point-of-care diagnosis in healthcare. Nitrocellulose has been the polymer predominantly used for membrane fabrication for these devices, but its instability and tendency to spontaneously decompose at a higher temperature, as well as inconsistent properties of the cellulose used as the raw feedstock, are drawbacks. Synthetic polymers have the potential to reduce the chances of material failure and the production of more reliable and reproducible membranes for this highly significant application field. Poly(methyl methacrylate) (PMMA) is one such polymer. It has previously been demonstrated that PMMA membranes with good thermal stability can be produced, and have potential for protein binding, which is a key attribute for materials suitable for use in immunoassay devices. However, the literature on PMMA membranes produced via air casting or other techniques is scarce and there are few demonstrations of lateral flow capability. The aim of this study was to develop a repeatable and robust methodology for production of PMMA membranes using an air casting approach with thermally induced phase separation (TIPS) of the polymer. A casting rig was designed and optimised for successful production of PMMA membranes on a commercial backing material. The influence of polymer loading, water content, and humidity on the PMMA membrane characteristics were also investigated. In addition, the effects of glycerol and poly(ethylene glycol) as individual additives on the membrane integrity and pore morphology were studied. The results show that the membrane morphology can be tailored by controlling the composition of the lacquer used for casting and the process parameters.

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Publications

In Preparation

N. Murphy, A. Rafferty, M. Morris, E. J. Flynn “Production of microporous PMMA membranes via a TIPS–air-casting method: Effect of polymer loading on pore morphology”

N. Murphy, A. Rafferty, M. Morris “Water effects on pore morphology of microporous PMMA membranes”

N. Murphy, A. Rafferty, M. Morris “Inducing nanoporous morphologies in PMMA membranes through the use of PEG”

Abbreviations

TIPS = Thermally induced phase separation

VIPS = Vapour sorption-induced phase separation

NIPS = Non-solvent-induced phase separation

PMMA = Poly (methy methacrylate)

PVDF = Polyvinylidene

NC = Nitrocellulose

PEG = Poly (ethylene glycol)

PS = Polystyrene

PDMS = Poly(Dimethylsiloxane)

PEO = Poly(ethylene oxide)

SDBS = Sodium dodecyl benzenesulfate

SSR = Solid-state relay

PID = Proportional integral derivative

RTD = Resistance thermometer detector

SEM = Scanning electron microscopy

GPC = Gel permeation chromatography

PDI = Polydispersity index

BET = Brunauer-Emmett-Teller

GPC = Gel permeation chromatography

NTU = Nephelometric turbidity unit

CFT = Capillary flow time

MPS = Mercury porosimetry

M_n = Number averaged molecular weight of polymer

M_w = Weight averaged molecular weight of polymer

T_g = Glass transition temperature ($^{\circ}\text{C}$)

χ = Flory-Huggins interactionparameter

D = Pore diameter (μm)

γ = Surface tension (N m^{-1})

θ = Contact angle ($^{\circ}$)

P = Hydraulic pressure (bar)

δ_d = Hansen dispersive force parameter

δ_p = Hansen dipole parameter

δ_h = Hansen hydrogen bonding parameter

V_m = molar volume ($\text{m}^3 \text{mol}^{-1}$)

R = universal gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)

T = Temperature in Kelvin (K)

C_p = Centipoise

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Chapter 1

Introduction

1.1 Membranes

Membranes are highly porous, selectively permeable barriers used in an increasing range of industries since the 1950s [1–4]. Applications include desalination and water purification, clinical diagnostics in the form of immunoassay devices, gas separation, colloid separation, and general filtration [1,4]. This broad range of uses results from the ability to control and tailor membrane morphology and pore size by varying process parameters (e.g., temperature and solution flow rate) during membrane synthesis and production. **Figure 1.1** summarises membrane types, filtration processes, porosity classes, and analytes associated with membrane pore size.

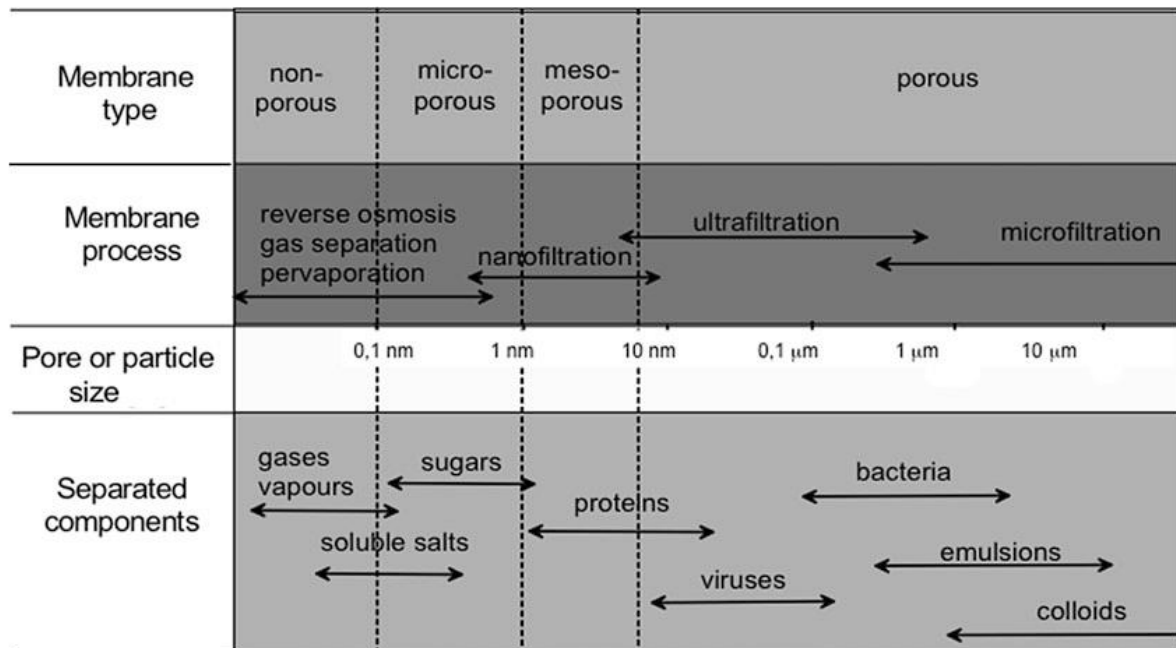


Figure 1.1 Summary of membrane types, separation mechanisms, typical pore sizes, and filtrates [5].

The pore size distribution of membranes can be classified as isotropic or anisotropic, with a symmetric or asymmetric membrane morphology [1], as shown in **Figure 1.2**.

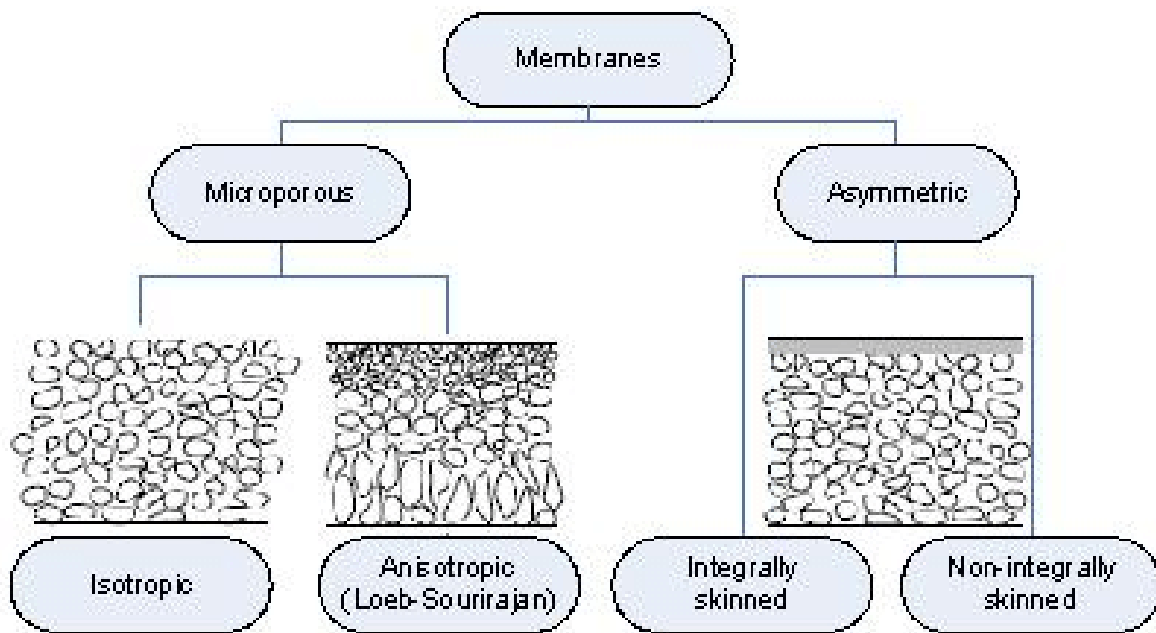


Figure 1.2 Membrane classification and structure [6].

Isotropic membranes have a symmetric, rigid and highly porous interconnected structure in which pores are randomly dispersed throughout. The pore size is generally uniform (monodisperse) or at least has a narrow pore size distribution (PSD) [7]. By contrast, anisotropic membranes have an almost layered structure with a varying porous structure throughout. Sometimes, a skin layer can develop that may be partly or entirely non-porous. The skin layer is supported by the underlying material and the pores throughout these types of membrane are highly varied with a wide PSD [7]. Membranes with integral skinning are produced during formation in processes such as phase inversion, whereas non-integrally skinned membranes involve secondary deposition processes on a porous support [6].

One application of membrane technology with increasing potential is in immunoassays for the measurement of a target analyte, such as a pathogen or biomarker in human clinical samples, or contaminants in water or foodstuffs [8–11]. Immunoassays are playing an increasing role in point-of-care diagnostics and are being investigated for use in COVID-19 detection, with some work showing promise in detecting diseases such as Ebola virus [12]. Other application examples include detection of cardiac troponins [13] as well as bacteria

[14] and viruses [15]. The assays are based on immunochemistry principles, whereby a target analyte is detected via an antibody–antigen reaction for which the antibody is labelled with a detectable dye to signal the presence or absence of the target analyte [8,16]. Immunoassay devices are relatively simple in design, as illustrated in **Figure 1.3**.

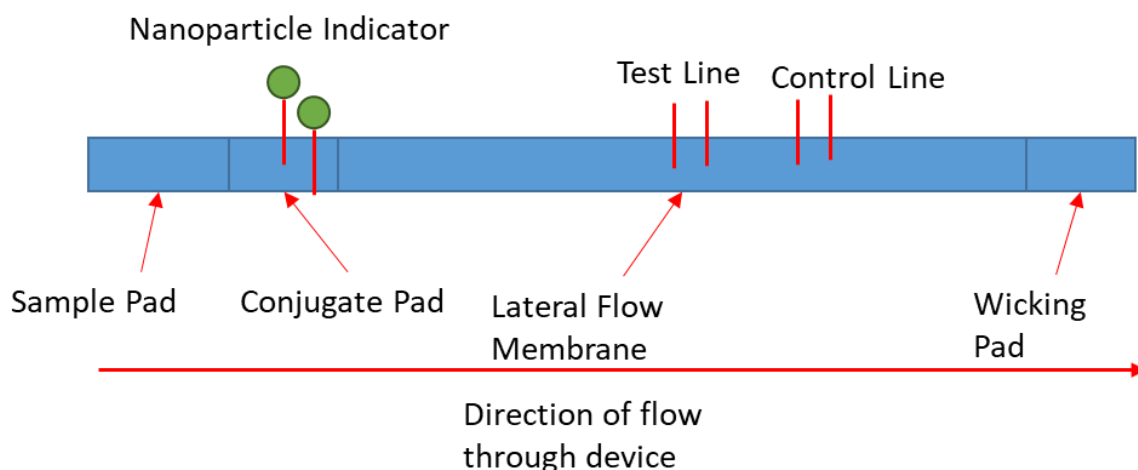
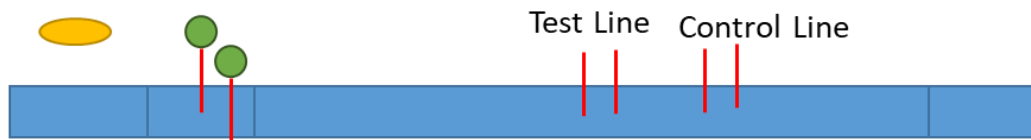


Figure 1.3 Architecture of a typical immunoassay device. As shown, sample flow through the membrane is in the lateral direction, which gives rise to the term “lateral flow membrane” [11].

The sample for analysis is placed on the sample pad and after wetting it migrates to the conjugate pad, where a nanoparticle indicator (typically colloidal gold or latex nanoparticles) attached to an antibody can bind to the target analyte if it is present in the sample. The sample then travels freely through the engineered pore structure of the lateral flow membrane until it reaches the test line and then the control line. The test line consists of immobilised proteins that bind to the nanoparticle indicator to generate a signal that reflects the presence of the analyte in the sample. The control line contains affinity ligands that bind the nanoparticle conjugate with or without the analyte to confirm that the assay is working correctly. After the control line, the sample flows into the wicking pad, which ensures consistent lateral flow across the test and control lines. This process is outlined in **Figure 1.4**.

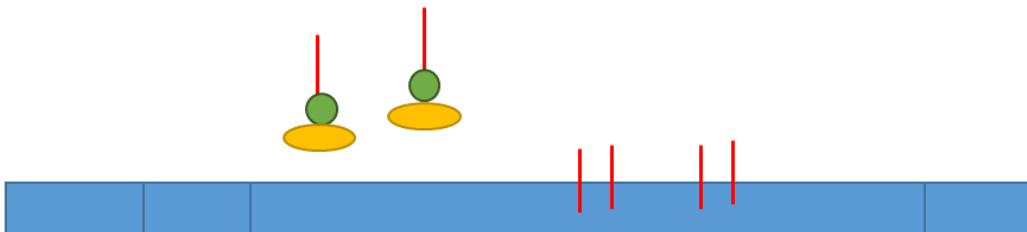
1. Sample added to device



2. Sample Binds to Indicator



3. Sample & nanoparticle are released



4. Nanoparticle bind to test line if target molecule present or control line if no target molecule is present

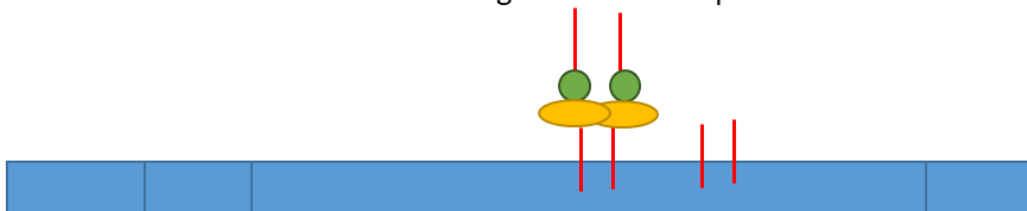


Figure 1.4 Schematic of the operation of a lateral flow immunoassay device.

The three most important components in immunoassay devices are the lateral flow membrane, the indicator, and the test line. Owing to the ability to alter and change these components, immunoassay devices can in theory be used for several assay types. However, the two main challenges are: (1) producing a consistent and reproducible lateral flow

membrane; and (2) refining target enzymes to allow testing for specific antibodies or antigens. The focus of the research carried out for this thesis was to address the first challenge, namely, to develop a robust and reproducible process for the fabrication of microporous membranes with a view to using them in lateral flow immunoassay devices.

This chapter outlines the theoretical considerations, challenges and techniques that can be utilised to fabricate membranes and provides a background to the experiments carried out that are described in Chapters 3–5.

1.2 Membrane materials

1.2.1 Nitrocellulose and cellulose

For commercial membranes the material most widely used for the better part of 70 years has been nitrocellulose (NC). NC is a cellulose derivative (**Figure 1.5**) manufactured by treating cellulose with a mixture of sulfuric acid and nitric acid [17]; in some instances, phosphoric or acetic acid [17] can be used in place of sulfuric acid.

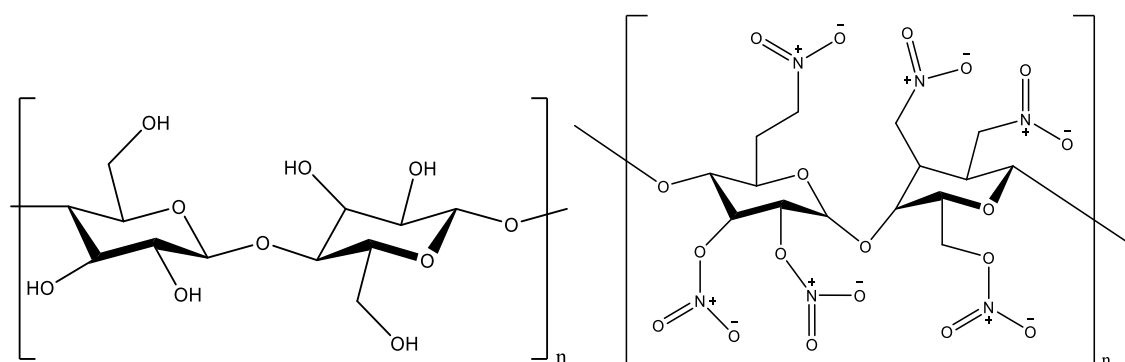


Figure 1.5 Structure of cellulose (left) and nitrocellulose (right).

Cellulose is a primary constituent of cell walls in plant materials. The main sources of cellulose for industrial use are wood and cotton; wood can contain 40–47% cellulose, depending on the species [17], while cotton spores can contain up to 95% cellulose [17].

However, NC has several disadvantages that limit its suitability for large-scale membrane production:

- NC can spontaneously decompose because the nitro groups are self-oxidising. While this is dependent on a high degree of nitration, the NC used for membrane production can also undergo this spontaneous decomposition [18].
- The nitro groups also mean that NC is highly flammable and in the case of higher degrees of nitration can even be highly explosive [19,20].

- As the raw cellulose for NC production is derived from plant material, commercial-scale farming can be affected by reduced crop yields as a result of external factors such as pests, insufficient watering [21,22], over-watering [23], crop density [24], disease [25], and severe weather [26,27].
- The energy inputs for raw plant matter are significant when water [28–30], fertilizer [31,32], pesticides [33], and machinery for sowing and harvesting are all accounted for.
- As it is a naturally occurring polymer, cellulose derived from plants can often have different chain lengths, which increases the polydispersity (PDI) and in turn leads to poorer phase control when casting membranes [34].
- The sulfuric, nitric, and sometimes acetic or phosphoric acids used in the nitration process can cause significant environmental damage and a significant amount of wastewater has to be treated after production [35].

Because of these issues, the development and deployment of new materials for lateral flow devices is a potentially valuable area of research.

1.2.2 Poly(methyl methacrylate)

Poly(methyl methacrylate) (PMMA; **Figure 1.6**) is a thermoplastic synthetic polymer that has long been of interest as a material for membrane fabrication [36–39]. PMMA research to date has centred on studying gas fluxes through PMMA membranes [36], the mechanisms underlying membrane formation [37–39], and use as cationic dye exchange membranes [40]. To the best of our knowledge, there has been very little research on PMMA viability as a lateral flow membrane for immunoassay diagnostics.

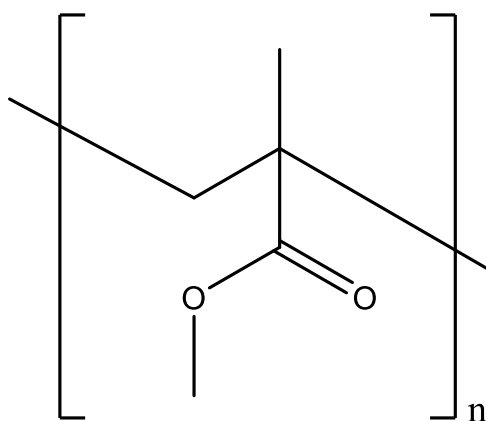


Figure 1.6 Structure of PMMA.

In comparison to NC, PMMA has a number of favourable properties: it is non-explosive and non-combustible and does not spontaneously degrade. Its acrylate side chain is suitable for a certain degree of protein absorption [41]. As PMMA is a synthetic polymer, the issues arising from the varying quality of cellulose and NC can be avoided, as PMMA can be synthesised with a desirable chain length and narrow, acceptable PDI ($PDI < 1.5$). Furthermore, it is possible to form porous membranes using PMMA, as first shown by Sakai and Tanzawa [42] in 1978 through the use of an immersion casting type of technique. Other researchers have also fabricated membranes using this method, such as Cheng et al. [36], Kuo et al. [43], and Matsuyama et al. [44]. In addition, Tsai and Torkelson have shown that PMMA membranes can also be fabricated through a solvent evaporation method [39]. More recent studies have focused on the production of mixed membranes, typically including poly(vinylidene fluoride) (PVDF) [45–47], polystyrene (PS) [48], poly(dimethylsiloxane) (PDMS) [49,50], and poly(ethylene oxide) (PEO) [51], while some composite membranes using ceramic additives have also been produced using SiO_2 [52], TiO_2 [53,54], and zeolites [55].

1.2.3 Microfluidics and microfluidic devices

Microfluidic devices analyse and handle small liquid volumes by confining the liquid to a small area of the order of nano- to micrometres. In simple terms, microfluidic devices deliver, mix, separate, react, or otherwise process small volumes of liquids, ranging from the femto- to microlitre range [56,57]. Microfluidic devices have been used for analyses in a variety of areas ranging from cellomics to environmental monitoring, lab-on-chip applications, and high-performance liquid chromatography [58,59]. Microfluidics can be fabricated from an array of materials ranging from ceramics to polymers, silicon, and glass, with each material having advantages and disadvantages according to its end use [59]. The function of a microfluidic device relies on zero energy input, in that the capillary forces between the liquid and device wall are what facilitate transport through the device. In contrast to macrofluidic behaviour, factors such as surface tension, energy dissipation, and fluidic resistance are amplified at a micro level, leading to them becoming the dominant forces that drive flow [57]. In cases with a channel size between 100 nm and 100 μm the Reynolds number is drastically reduced, resulting in laminar flow instead of the expected turbulent flow observed at a macro scale [56]. It is phenomena such as this laminar flow that are exploited and lead to the many uses for microfluidic devices. As membranes can often require fluids at a microlitre scale for the reaction and/or analysis for which they are being used, they can also be thought of as microfluidic devices while also exploiting the phenomena that occur at a micro scale [56,60].

PMMA has already attracted interest as a material for microfluidic devices, with recent developments looking at 3D printing and laser etching to produce micron-scale fluidic channels [61,62]. Another factor explaining the interest in PMMA as a microfluidic material is its relatively low cost of $<\text{€}10 \text{ kg}^{-1}$ [61].

1.3 Membrane fabrication

1.3.1 Phase separation

Polymer membranes are generally manufactured by casting a polymer solution in the presence of porogens onto a backing support, after which phase separation of the solution is induced [1,63,64]. Phase separation is the spontaneous demixing of a homogeneous solution into a heterogeneous solution containing two or more phases. In the case of polymers, this demixing leads to a polymer-rich, solvent-lean layer and a polymer-lean, solvent-rich layer [65]. This phenomenon is shown schematically in **Figure 1.7**.

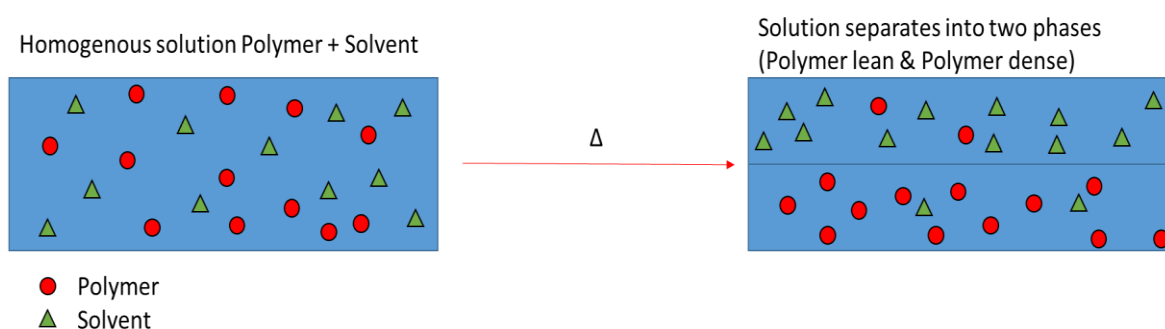


Figure 1.7 Representation of demixing in a polymer–solvent solution.

This demixing phenomenon can be related to a phase diagram for the solution, as shown in **Figure 1.8**. In the phase diagram, the one-phase region is above the binodal curve and represents the temperatures and concentrations at which the polymer remains in solution. The two-phase region is below the spinodal curve and represents the temperatures and concentrations at which the polymer will nucleate and cease to be in solution. The region in between these two curves is a metastable region, where polymer nucleation and membrane formation can be induced, and pore refinement can be achieved.

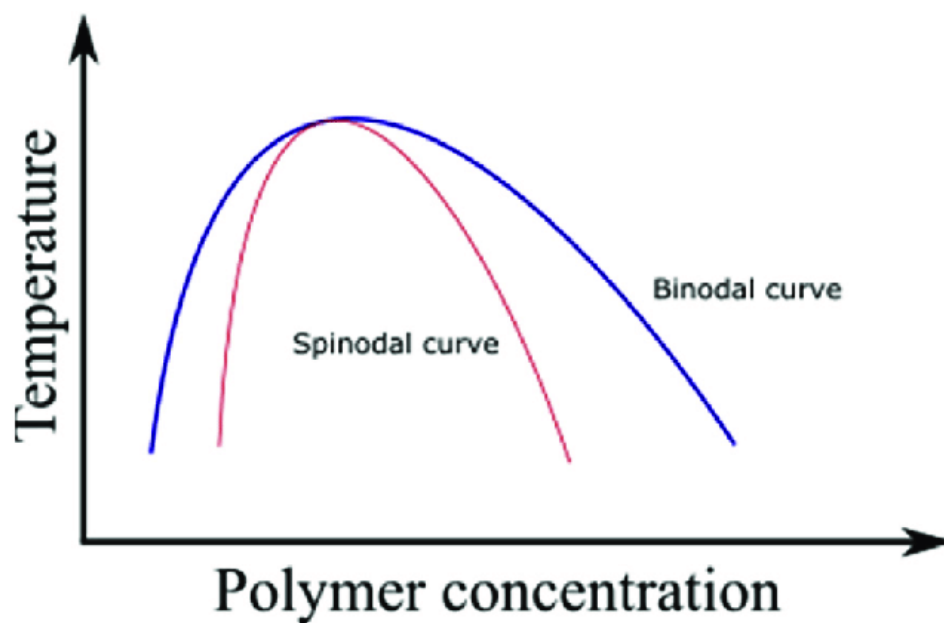


Figure 1.8 Phase diagram showing binodal and spinodal curves[66].

In most cases, a non-solvent (acts as or part of the porogen) is included in the polymer solution and a ternary phase diagram is used to determine the spinodal and binodal curves, as well as the various phases that can exist in such systems. This has been described in detail by Keshavarz et al. [67]. A representative diagram is presented in **Figure 1.9**.

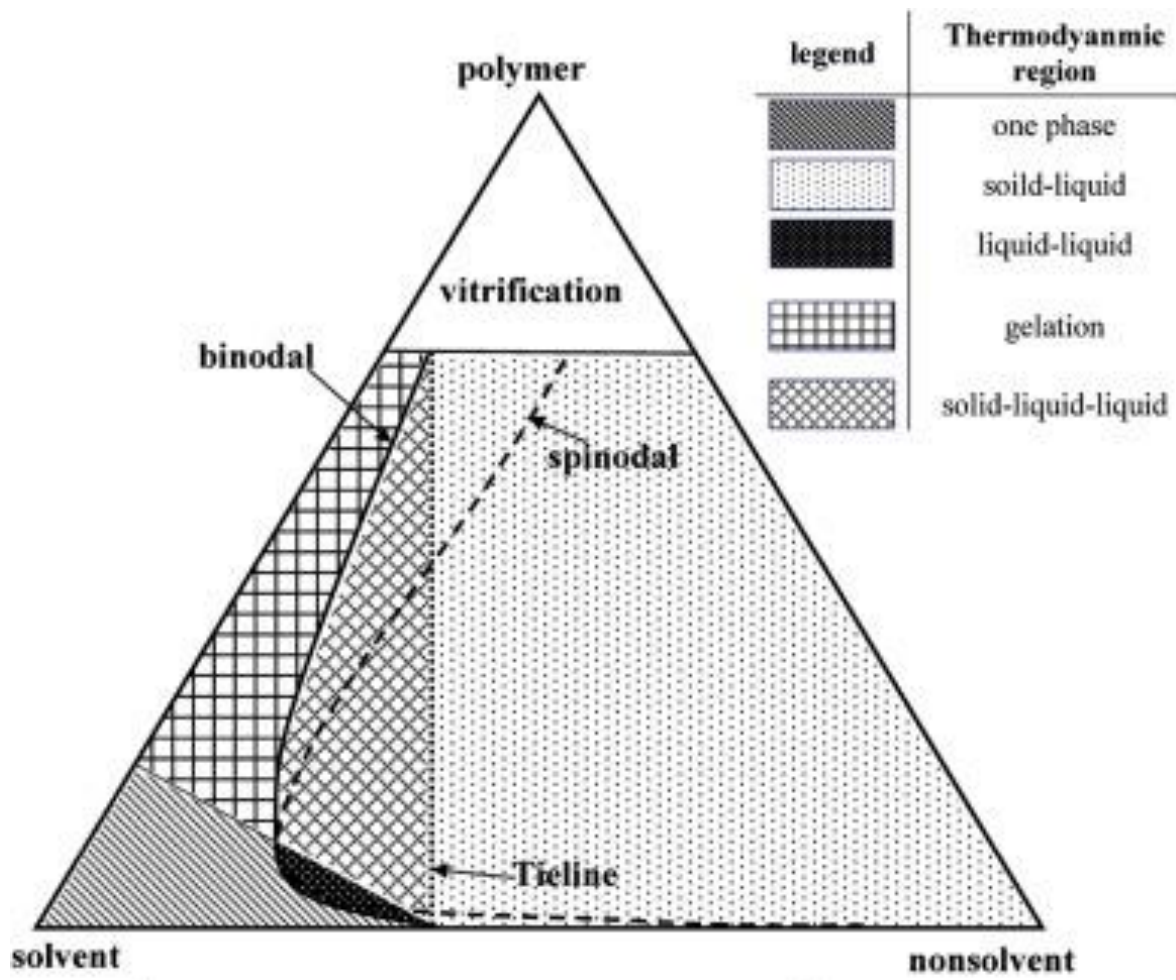


Figure 1.9 Phase diagram for a ternary system showing phase boundaries and binodal and spinodal curves [67].

For ternary systems, regions such as the gelation boundary, solid-liquid-liquid interface, and vitrification boundaries can be identified. By using such diagrams, it is possible to formulate a polymer solution for which phase separation can be rapidly induced by small changes in composition and refinement of the pore network can be achieved.

There are four methods that can be used to induce demixing [68]:

- Decreasing the solution temperature;
- Immersing the solution into a non-solvent bath;
- Exposing the solution to non-solvent vapour; and
- Allowing the solvent to evaporate.

These four methods have all been used to produce membranes and can be broken down into two categories: wet casting and dry casting. Wet casting is any process whereby the polymer solution is immersed in a non-solvent solution to induce phase separation, while dry casting is any process whereby air or vapour is used to induce phase separation. In addition, thermally induced phase separation (TIPS) can be used in both wet and dry casting process, whereby the temperature of either the immersion bath or casting bed is controlled to help in initiating the phase separation process.

1.3.2 Cloud point

The nucleation point for a polymer, which corresponds to crossing of the binodal curve in the phase diagram, can be thought of as the cloud point. While strictly speaking the cloud point is defined as the temperature or non-solvent concentration at which a 1% w/w polymer solution becomes turbid due to the onset of phase separation, in practice, any change in turbidity due to a change in temperature or non-solvent concentration can be deemed the cloud point of a given solution [69].

The two most common methods for determining the cloud point of a lacquer are titration with a non-solvent [70,71] and tracking the turbidity as the temperature changes [2].

1.3.3 Membrane and pore network formation

The mechanism underlying the formation of a membrane and its pore network is either spinodal decomposition or nucleation and growth.

Spinodal decomposition occurs when a system crosses the spinodal curve in the phase diagram (**Figure 1.8** and **Figure 1.9**), after which spontaneous phase separation will occur; in this case there is no nucleation step [72]. Phase separation is a rapid process and requires no nucleation site, so phase separation can be observed throughout the solution.

By contrast, a slower phase separation process occurs in membrane formation via nucleation and growth. In this case the system crosses the binodal curve in the phase diagram but does not cross the spinodal curve, and thus remains in the metastable region between both curves (**Figure 1.8** and **Figure 1.9**). Nucleation occurs throughout the system once the activation energy for nucleation has been achieved [73].

While both methods can lead to membrane formation, the mechanism underlying formation of the pore network is system-dependent, with polymer concentration being a critical factor in determining which mechanism occurs. A lower polymer concentration leads to the nucleation and growth route, while a higher concentration will lead to spinodal decomposition [73].

1.3.4 Casting methods

Immersion casting generally involves the casting of a two-phase lacquer containing a polymer and a solvent onto a support backing, after which the cast is immersed in a bath containing an appropriate non-solvent. Following removal from the bath, the cast is finally dried to leave the final membrane. The process is shown schematically in **Figure 1.10**.

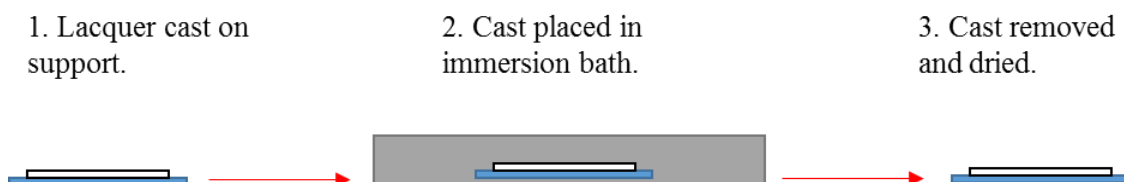


Figure 1.10 General process for immersion casting.

Overall, the general mechanism involves migration of the solvent in the lacquer mix through the polymer mix to form a two-phase system (polymer-lean phase and polymer-dense phase) as outlined in **Figure 1.7**. This migration is generally what drives the pore formation process. The morphology and the pore size and properties can typically be controlled by varying the temperature of the immersion bath.

Air casting, by contrast, uses a single lacquer that contains the polymer, a solvent, and, depending on the method for phase separation, a non-solvent. After the lacquer has been cast onto the backing and support, it is exposed to air so that the solvents are allowed to evaporate to form the membrane (**Figure 1.11**). There are two main ways in which phase separation is driven in this process: vapour-induced phase separation (VIPS) and non-solvent-induced phase separation (NIPS).

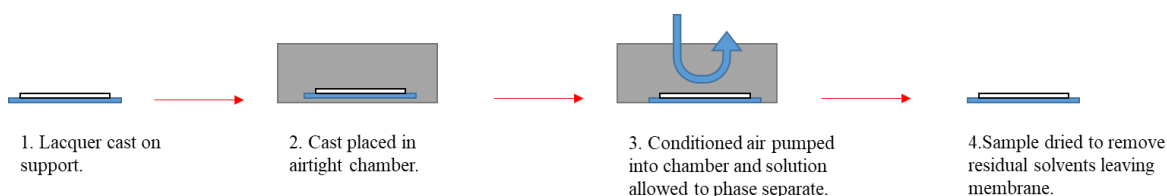


Figure 1.11 Visual representation of the air cast process.

In VIPS the cast lacquer is allowed to sit in an environment containing non-solvent vapour; this approach is mainly used when water is the non-solvent for the system [74,75]. The water vapour interacts at the surface of the polymer solution, allowing the formation of a localised polymer-lean layer, which drives phase separation. Typically, lacquers formulated for this process contain a solvent and the polymer; however, in some cases a non-solvent may be added in order to increase or improve phase separation. Phase separation in this instance is illustrated in **Figure 1.12**.

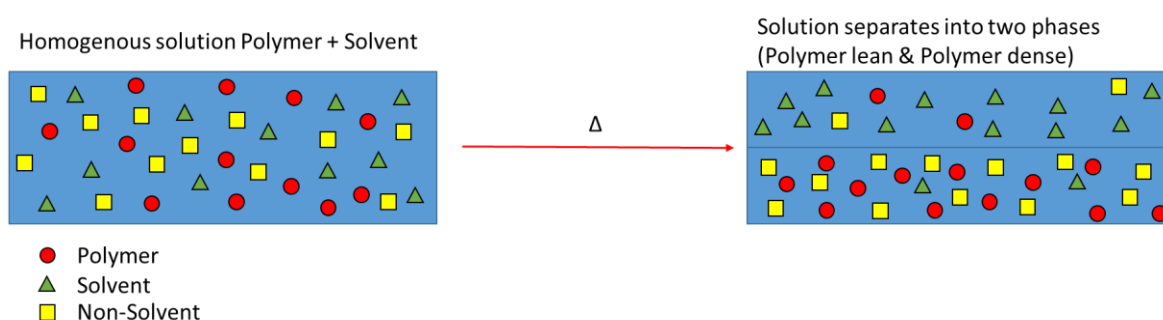


Figure 1.12 Visual representation of phase separation when a non-volatile non-solvent is included in the solvent mix.

By contrast, NIPS uses a polymer solution that includes a solvent, a non-solvent, and a polymer. The predominant force that drives the process is evaporation of the solvent, leaving the polymer and non-solvent in the polymer-dense layer. The non-solvent acts as a porogen: as it subsequently evaporates from the polymer-dense layer, it leaves behind pores in the resulting membrane.

By exploiting knowledge of the cloud point, it is possible to incorporate TIPS, whereby a lacquer solution containing a solvent, a non-solvent, and the polymer can be cast at a temperature below the cloud point, with phase separation induced via subsequent control of the temperature. Figure 1.13 shows a schematic of the TIPS–air casting approach.

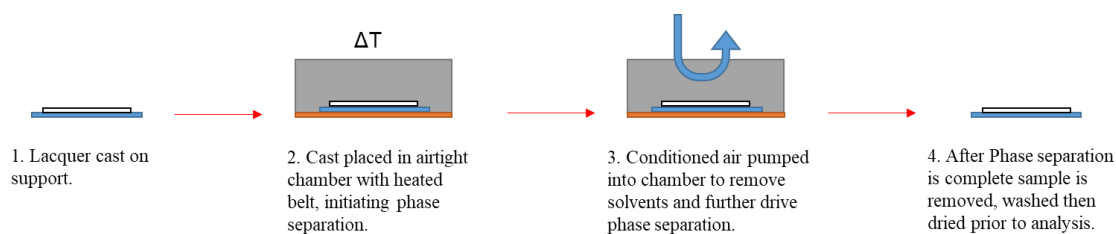


Figure 1.13 Visual representation of the TIPS–air casting process.

1.4 Membrane anomalies and modifications

Anomalies can often arise during membrane formation, the most frequent of which are skin layers and the formation of macrovoids. Membrane modification can be achieved by adding other polymers or chemicals to the solution, the most common of which are plasticisers and cross-linking agents.

1.4.1 Skin layers

Skin layers were mentioned in Section 1.1 and can be a common feature in anisotropic membranes; they are dense, nonporous polymer films that typically form at the interface between the casting solution and the air interface, and the non-solvent interface for air-cast and immersion-cast membranes, respectively. Skin layer development is primarily driven by the diffusion rate of the solvent and non-solvent through the polymer matrix as phase inversion occurs. The polymer precipitates as a swollen gel, and as the solvent and non-solvent diffuse they can carry excess polymer towards the surface. This results in a region with a high concentration of polymer, which leads to a densely packed and non-porous region [76]. As skin layers are densely packed, they can limit liquid uptake and flow of liquid through the pore network in the membrane and are therefore undesirable.

1.4.2 Macrovoids

Macrovoids are large voids that can form within a pore network. They are typically seen in the upper regions of membranes and can be described as finger-like in appearance. Macrovoids are particularly undesirable as they can lead to mechanical breakdown of the membrane and affect the through-flow of liquids. There are two theories on how macrovoids are formed. Reuvers [77] proposed that rapid liquid–liquid demixing results in a nucleation

site in the polymer-lean region, which then grows down into the bulk polymer due to diffusion of the solvent and non-solvent.

Shojaie et al. [78,79] hypothesised that diffusion facilitates macrovoid growth, as they observed that macrovoid growth occurred over a short space of time (2–5 seconds). They proposed an alternative hypothesis that the growth of nuclei into macrovoids is due to solutocapillary convection, which is induced by a higher non-solvent concentration at the liquid–vapour interface, that is, the area from which the solvent is evaporating. This will create a surface tension gradient that pulls the growing macrovoid into the solvent-rich environment. Thus, macrovoids are induced by convection diffusion due to the bulk flow initiated by interfacial convection [78,79].

While problematic, the formation of these structures can be minimised by limiting the thickness of the cast film and using delayed demixing of the cast solution by designing an appropriate solvent–non-solvent mix.

1.4.3 Plasticisers

Plasticisers are most commonly low-molecular-weight organic compounds that induce plasticisation of a polymer, that is, they lead to a more plastic-like polymer by making it softer and more flexible. In terms of the material properties, plasticisers can decrease the glass transition, crystallisation, and melting temperatures of a polymer, in turn increasing the polymer flexibility, and allow a greater degree of freedom in long-chain polymers by reducing mechanical rigidity and increasing chain mobility [80,81]. There are other polymer properties that plasticisers can affect as an additive, but the three aforementioned are the main properties that are desirable for lateral flow membranes. One of the most frequent reasons for using a plasticiser is to improve the mechanical strength of membranes that are brittle and flaky.

1.5 Lateral flow theory and capillary flow

Solute flow through a lateral flow membrane involves capillary flow through the interconnected pore network. Capillary flow is determined by the surface tension, which is related to the viscosity of the liquid, which in turn is linked to the attractive intermolecular forces in the liquid (**Figure 1.14**). Factors such as the nature of the liquid and the membrane also affect liquid flow in the membrane. The most influential factor is the presence of charged species on the membrane material, which in turn will affect the hydrophilicity or hydrophobicity of the membrane.

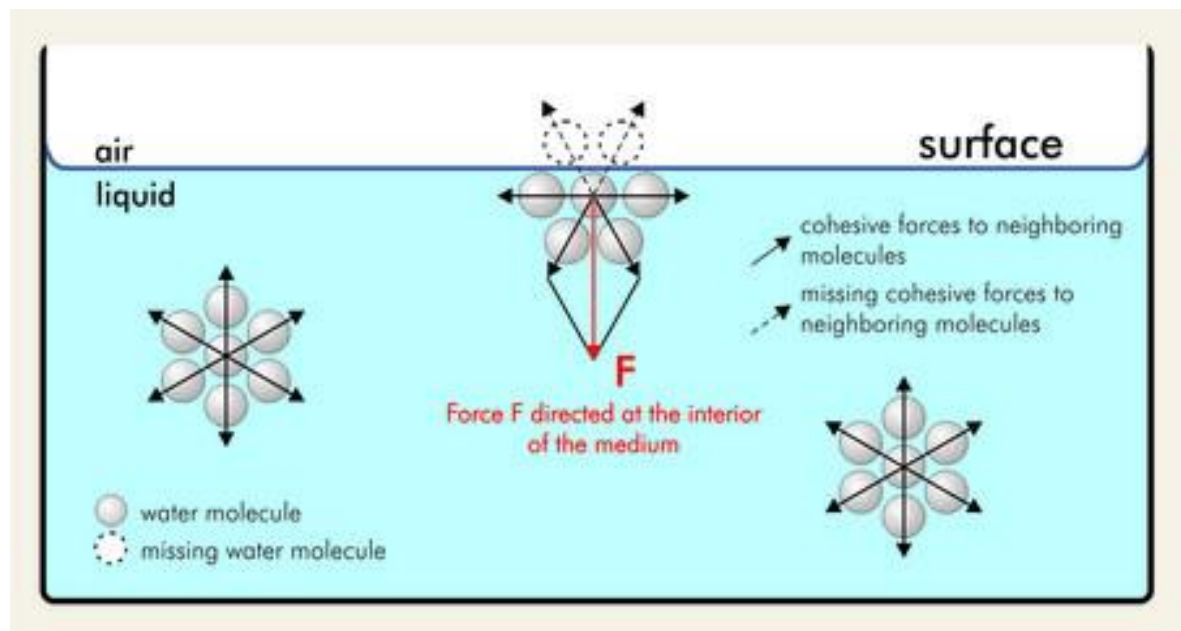


Figure 1.14 Intermolecular forces in a liquid [82].

As illustrated in **Figure 1.14**, a molecule in a liquid exhibits attraction in equal directions. However, for molecules at the surface there are no forces experienced above the surface of the liquid, so the net force of these surface molecules is directed into the interior of the liquid. In addition to the cohesive forces between molecules, there is also an adhesive force between the liquid and the vessel wall. This results in a concave surface on the liquid, which in turn reduces the surface tension [83]. Flow through a capillary occurs when the adhesive forces

between the liquid and the capillary wall are greater than the cohesive forces between molecules. This can be calculated according to the following equation:

$$h = \frac{2\gamma \cos(\theta)}{\rho g r}, \quad \text{Equation 1}$$

where:

- h is the height the liquid travels;
- γ is the surface tension of the liquid;
- θ is the contact angle between the liquid and the wall;
- ρ is the density of the liquid;
- g is acceleration due to gravity; and
- r is the radius of the tube.

In general, the narrower the tube, the more the liquid will rise, as shown in **Figure 1.15**, because of the increase in the influence of adhesive forces.

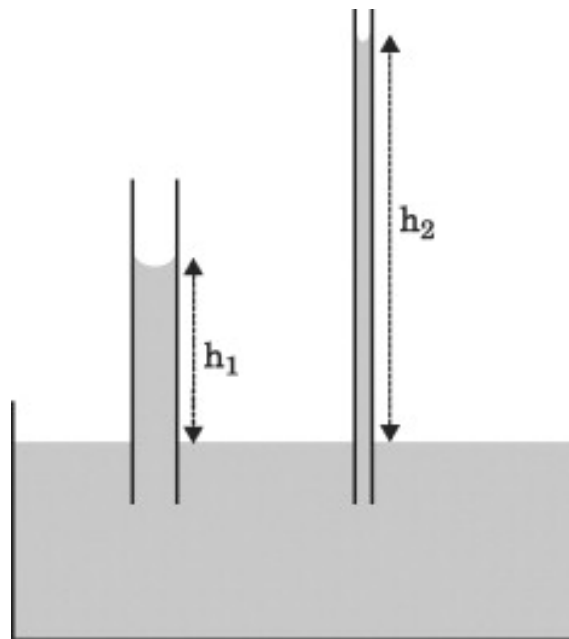


Figure 1.15 Capillary flow in a narrow tube [84].

The Washburn equation is also applicable for a membrane as it describes capillary flow in a bundle of parallel cylindrical tubes, which are comparable to the interconnected pores in a membrane [85]. Like **Equation 1**, it can be used to predict the penetration length of liquid into a membrane, according to:

$$L = \sqrt{\frac{\gamma r t \cos(\phi)}{2\eta}}, \quad \text{Equation 2}$$

where:

- L is the penetration length of the liquid;
- γ is the surface tension of the liquid;
- η is the dynamic viscosity;
- R is the universal gas constant;
- T is the absolute temperature; and
- ϕ is the contact angle between the liquid and the wall.

However, it should be noted that when using the Washburn equation, any predictions will be in the absence of gravity and it is assumed that the capillary has a constant radius.

In order to overcome the shortcomings of Washburn's original work, specifically, Washburn assumes that the liquid is an incompressible Newtonian fluid, and that heterogeneous media and complex pore and channel structures are more typical real-world situations], recent studies have focused on alterations to and derivations of the equation to allow far more robust methods for making predictions and accounting for different media interactions [86]. In the case of membranes, the most applicable are perhaps the studies by Cai et al. [87] and Feng et al. [88], which deal with tortuous structures and the viscosity and slippage of liquids, respectively. Such modifications of the classical Washburn equation can be applied to

account for the complex geometry of membranes and the effect of gravity through slippage for more appropriate modelling.

1.6 Hansen solubility parameters, the Flory–Huggins model, and solvent choice

1.6.1 Hansen solubility parameters

The Hansen methodology for assessing the solubility of one material in another is derived from the simplified approach first developed by Hildebrand [89]. The approach is based on the premise that “like will dissolve like”. In the model, Hildebrand proposed that molecules, solvents and polymers, etc. with similar cohesive energies will be mutually soluble. The *cohesive energy* of a system is the energy required to separate constituent molecules from a system [81]. The term *solubility parameter* was used to reflect the difference in cohesive energy. Hansen, a student of Hildebrand, recognised that the Hildebrand solubility parameter could be broken into three constituent solubility parameters to provide a method for determining the solubility of a polymer in a potential solvent. The same “like will dissolve like” premise is applied, with values assigned to three types of intermolecular force:

- δ_D : dispersive forces between molecules;
- δ_P : dipole interactions between molecules; and
- δ_H : hydrogen bonding between molecules.

In addition, polymers are assigned an interaction radius R_0 .

Values for these three Hansen parameters can be used as coordinates for a plot in 3D space along with the interaction radius R for a sphere, as shown in **Figure 1.16** for PMMA and the solvents tetrahydrofuran (THF), acetone, ethanol, butanol, and methanol. This 3D space is commonly referred to as Hansen space.

Common Solvents & PMMA Plotted in Hansen Space

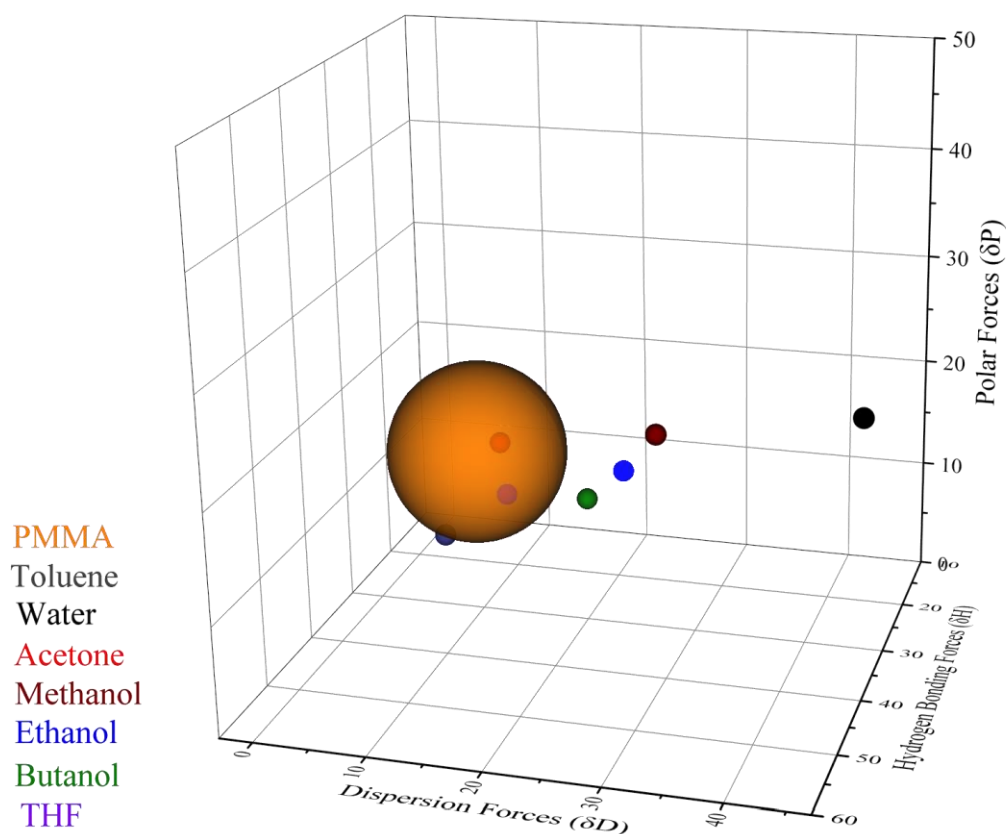


Figure 1.16 Various solvents and PMMA plotted in Hansen space.

Mathematically, the distance between a polymer and solvent (R_a) can be calculated according to:

$$(R_a)^2 = 4(\delta_{D2} - \delta_{D1})^2 + (\delta_{P2} + \delta_{P1})^2 + (\delta_{H2} + \delta_{H1})^2, \quad \text{Equation 3}$$

where subscript 2 denotes the polymer and subscript 1 denotes the solvent.

By combining the calculated distance between molecules and the interaction radius of the polymer, the relative energy difference (RED) can be determined:

$$\text{RED} = \frac{R_a}{R_0}. \quad \text{Equation 4}$$

The RED value indicates the suitability of a solvent for a given polymer:

- For $RED < 1$, the polymer will dissolve;
- For $RED = 1$, the polymer will partially dissolve; and
- For $RED > 1$, the polymer will not dissolve.

In addition, the parameters for a solvent mixture can be calculated by applying a partial parameter approach [90,91], whereby the contribution of an individual component to dispersive, dipole, and hydrogen bonding forces is calculated according to its ratio in the overall mixture. This approach is particularly useful for systems containing a solvent and a non-solvent that permit dissolution and precipitation of a polymer. However, it should be noted that the parameters will vary with the temperature and the molecular chain length and that the parameters are hard to measure. Further work by Abbott et al. addressed these issues [91], but the parameters should nonetheless only be used as approximations and should not be taken as absolute values.

Lindvig et al. [92] devised a method using the Hansen solubility parameters to determine the Flory–Huggins parameter χ for a polymer–solvent system. By combining both methods, a relatively reliable approximation for χ can be achieved and a suitable solvent system for a polymer system can be designed. This approach is particularly useful when designing a solvent system for use in a TIPS–air casting process, as both the solvent and non-solvent can be chosen such that phase separation can be rapidly induced by reducing the temperature.

The equation used to calculate χ is adapted from the regular solution relationship between the Flory–Huggins parameter and the solubility parameter:

$$\chi_{12} = \frac{V_1(\delta_1 - \delta_2)^2}{RT}, \quad \text{Equation 5}$$

where:

- χ_{12} is the mixing parameter;
- V_1 is the molar volume of the solvent;
- δ_1 is the Hildebrand solubility parameter of the solvent;
- δ_2 is the Hildebrand solubility parameter of the polymer;
- R is the universal gas constant; and
- T is the absolute temperature.

By replacing the Hildebrand parameter with Hansen parameters, the model can account for polar and hydrogen bonding forces, which the Hildebrand parameters fail to account for [92].

By substituting **Equation 3** in place of the Hildebrand parameters in **Equation 5** and including the correction parameter α , χ can be calculated:

$$\chi_{12} = \alpha \frac{V_1(4(\delta_{d2}-\delta_{d1})^2 + (\delta_{p2}+\delta_{p1})^2 + (\delta_{h2}+\delta_{h1})^2)}{RT}. \quad \text{Equation 6}$$

It should be noted, however, that the method is sensitive to variations in the Hansen solubility parameters, which vary in the literature. In addition, Lindvig et al. [92] point out that while Hansen suggests $\alpha = 1$ for solutions in which dispersion forces dominate the interactions, their previous study [93] revealed that results for χ in the case of polyacrylates, methacrylates, and poly(vinyl acetates) are overestimated, which suggests that better results may be obtained for $\alpha < 1$. However, for the purposes of approximating χ for a suitable solvent system to be used in an air casting–TIPS system, the use of $\alpha = 1$ is sufficient.

1.7 Summary and thesis outline

The production of lateral flow membranes is a complex and challenging process to control fully. Current immunoassays mainly use NC as the membrane material, but NC has several disadvantages for large-scale membrane production. PMMA is another polymer with potential applicability in lateral flow membranes. The work carried out in this study aimed to identify a robust method for the manufacture of PMMA lateral-flow membranes using an air cast-TIPS process.

This chapter has described the theoretical background for the concepts and principles applied in the experimental work. The remainder of the thesis is organised as follows.

Chapter 2 details the construction of a suitable apparatus that adequately combines elements required for the TIPS and air casting approaches.

Chapter 3 details the development of the air casting method and characterisation of the casting solutions. Casting solutions were characterised by varying the temperature and measuring the turbidity of the solution. Membranes were characterised using scanning electron microscopy (SEM), mercury porosimetry, BET analysis, and measurement of capillary flow times.

Chapter 4 describes the effects of water and humidity on the pore morphology. The effect of humidity was determined by varying the relative humidity of the air supply used during membrane curing. In separate experiments, the effect of water addition to the casting solution was investigated. Casting solutions and membranes were characterised in the same manner as mentioned for Chapter 3.

Chapter 5 describes an investigation of two approaches for modification of PMMA membranes: plasticisation via glycerol addition and use of poly(ethylene glycol) as a

sacrificial porogen added to the casting solution. Casting solutions and membranes were characterised as outlined for Chapter 3.

Chapter 6 outlines future work that could follow on from the research findings from this study.

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Chapter 2

Development of the Air casting Apparatus

2.1 Introduction

To prepare membranes reliably and reproducibly, a robust preparation method and apparatus are needed. Air casting of membranes is a challenge because the casting environment needs precise control. In this study, a casting apparatus was designed and built. In building an air casting apparatus, several factors needed to be considered:

1. The bed on which the lacquer is cast
2. Air delivery to the chambers
3. Control of humidity within the chambers
4. Delivery of lacquer onto a support
5. Data logging devices for measurement and control of various parameters.

All of the above factors were scoped, and a cost-effective solution was identified for each one. The initial design for the proposed apparatus is shown in Figure 2.1.

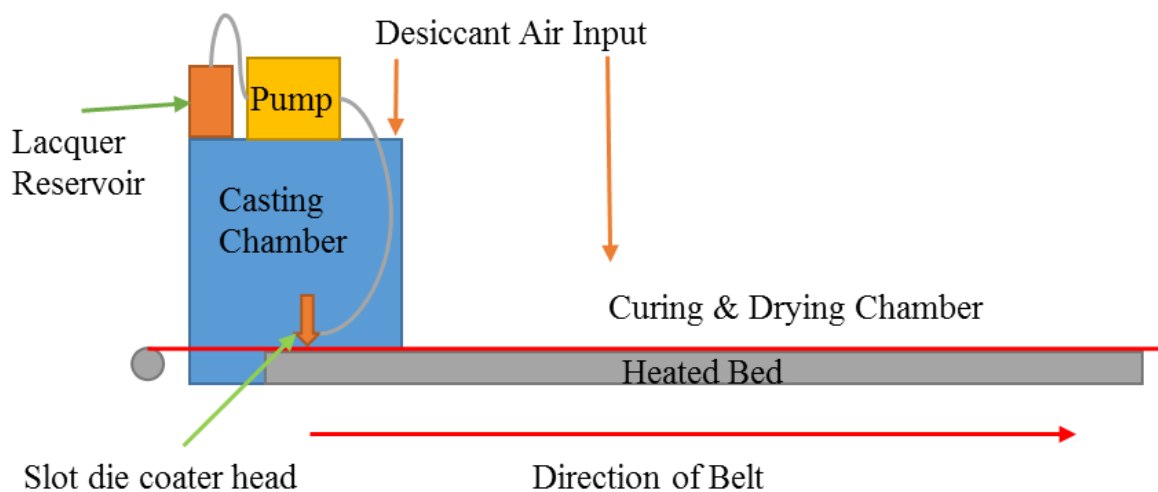


Figure 2.1: Schematic of the proposed air casting apparatus. See text for details.

By controlling the casting parameters, it should be possible to exert control of the pore morphology of membranes [1]. In addition, by manipulating the pump speed and belt speed, the membrane thickness can be controlled.

2.2 Heated bed

As outlined in Chapter 1, phase separation in air casting methods tends to be driven by either VIPS or TIPS. The stability of the bed temperature is crucial in order to drive phase separation via TIPS. For the proposed air casting–TIPS apparatus, the bed was designed as an array of aluminium plates with copper piping running through the centre. Water is pumped through the pipes. Owing the high specific heat capacity of water and aluminium and the low specific heat capacity of copper (4177.4 , 903 , and $494 \text{ J kg}^{-1} \text{ K}^{-1}$, respectively [2]), minimal thermal loss is observed. Liquid cooling plates were purchased from Farnell and a solid mockup was prepared using the components shown in **Figure 2.2**.

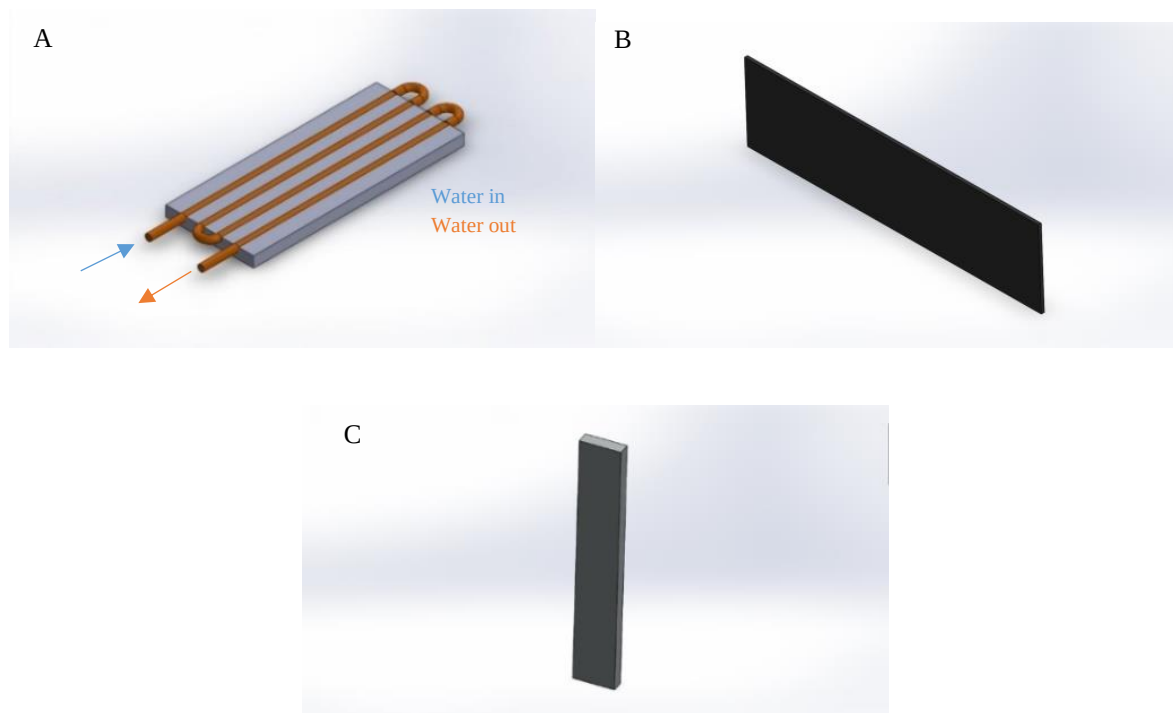


Figure 2.2: Solidworks renderings of the bed components: (A) liquid heating plate, (B) nylon insulating sheet, and (C) milled aluminium bed spacer.

An array of liquid cooling plates was required to span the length of the casting bed. Two milled aluminium dividers were added to the array in order to permit clearance and space for aluminium struts and acrylic panelling to divide each chamber. The assembled array was mounted on a polycarbonate sheet, as shown in **Figure 2.3**, to allow levelling of the bed

before installation. The constructed bed was then installed on a stainless-steel plate that acts as the floor of the chamber assembly.

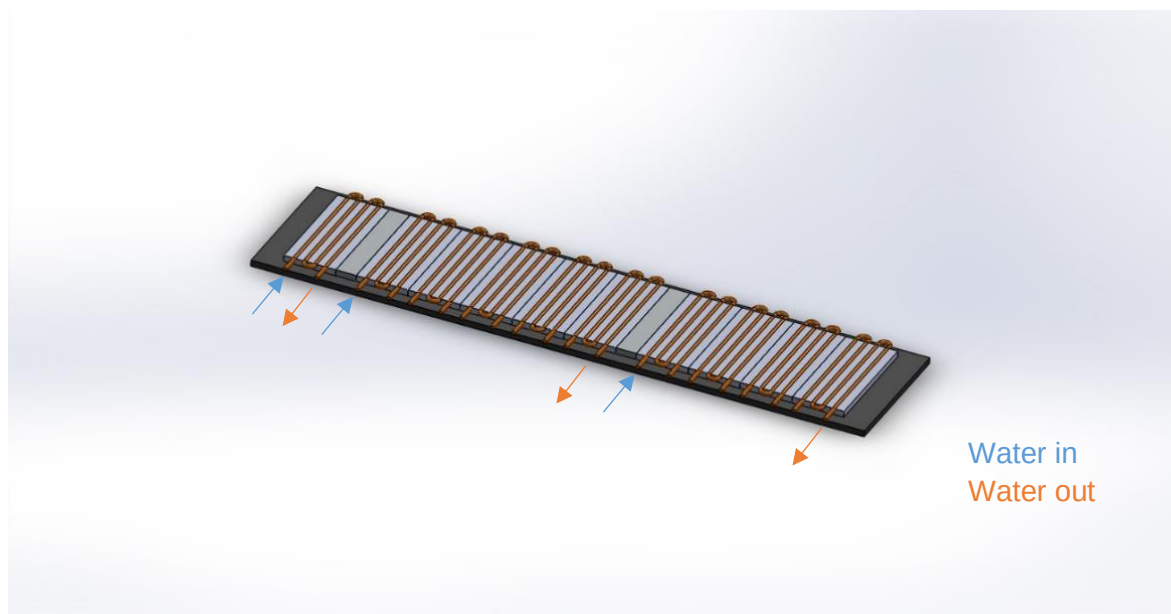


Figure 2.3: Heated bed array.

The bed is divided into three sections: casting, curing, and drying sections, each of which can be independently controlled. The temperature was controlled via water heating using a Grant JBA 5 Academy water bath. The heated water was circulated through the copper pipes using a KNF NF300 KT.18s diaphragm pump as outlined in **Figure 2.2A**. For longer sections containing multiple heating plates as shown in **Figure 2.3**, plates were connected in series using hosing, with water entering from the left and draining from the right. All hosing was secured in place using jubilee clips to eliminate any risk of leaks. Bed temperatures were monitored using a Pico Technology TC-08 eight-channel logger and K-type thermocouples.

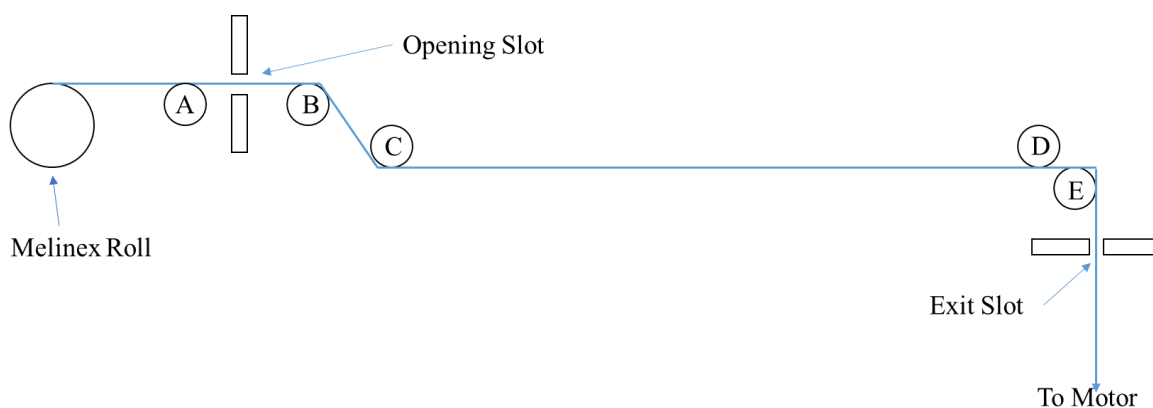


Figure 2.4: Schematic of the Melinex path through the air casting rig.

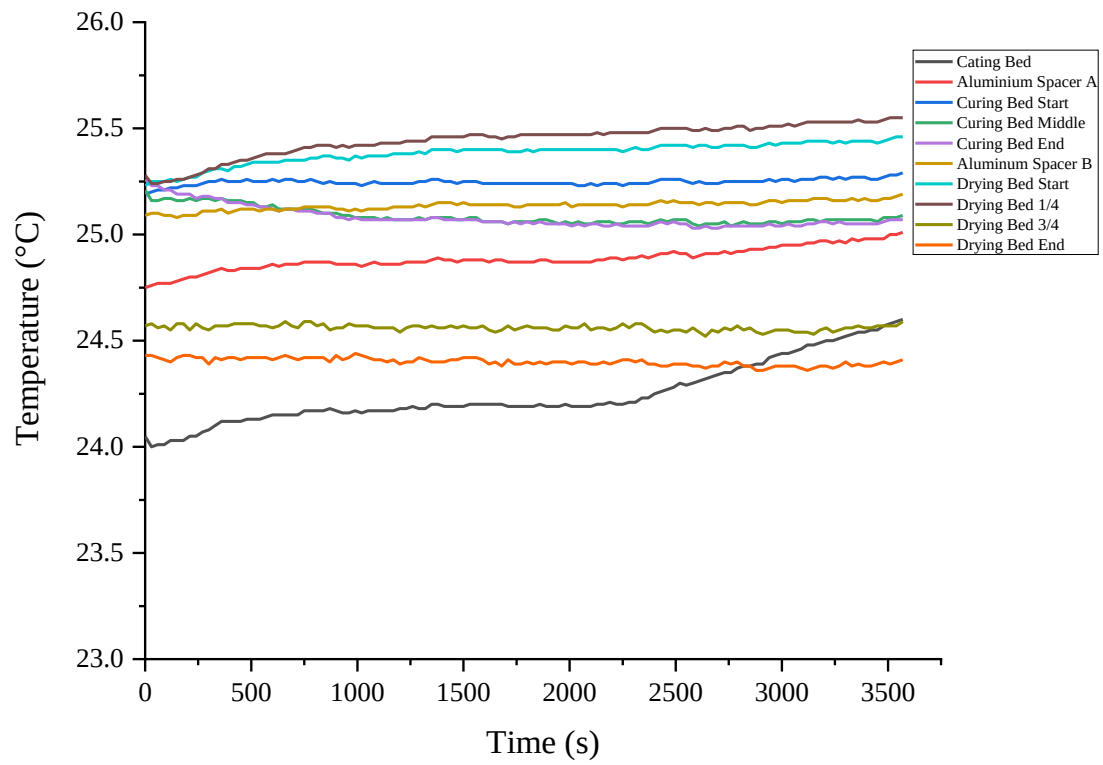
The Melinex film used to support membranes (i.e. membranes are cast onto the film rather directly on a bed and lifted off) is mounted and fed through the machine as outlined in **Figure 2.4**. The rollers (labelled A–E) allow the Melinex to pass over the heated bed with ease without any stress. Stress on the Melinex could lead to defects in the membranes because of tension between the Melinex mount and the motor.

Rollers A and B bring the Melinex through the opening slot to the casting chamber, roller C brings the Melinex in line with the height of the heated bed, and rollers D and E bring the Melinex through the exit slot and in line with the motor.

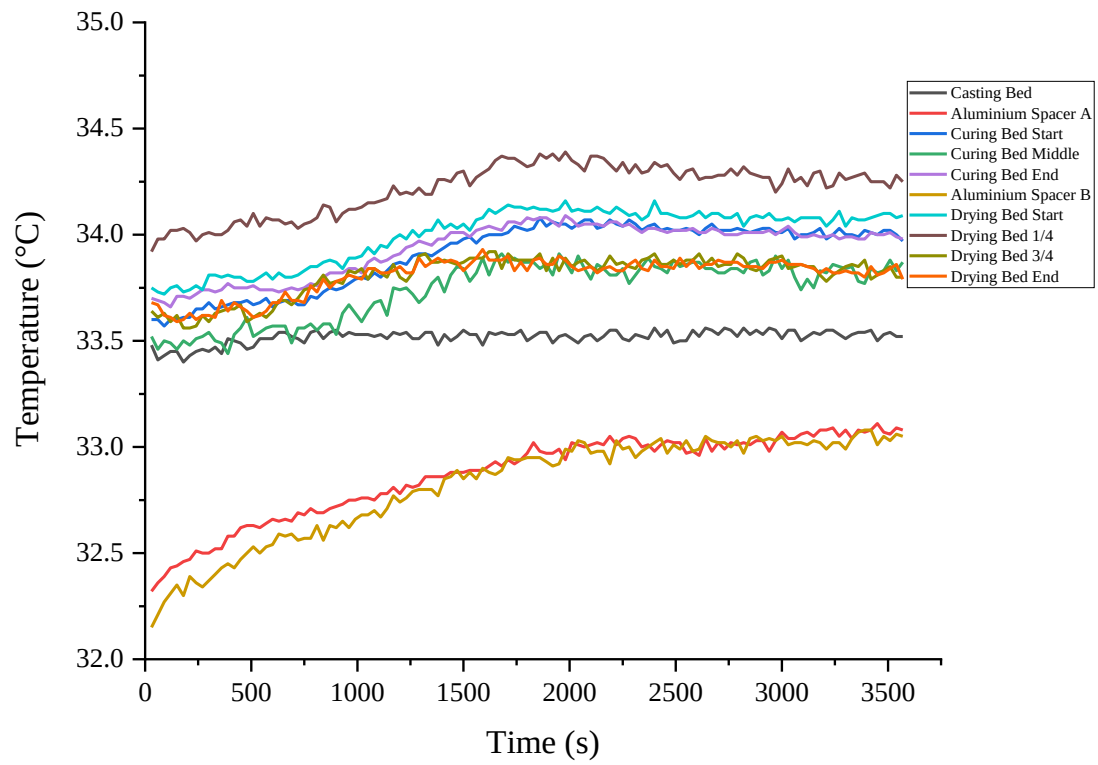
Figure 2.5 shows the bed temperature logged over 3600 s at 30 s intervals using K-type thermocouples spread along the heated bed and aluminium spacers during circulation of heated water. Stability measurements were carried out at set temperatures of 25, 35, and 45 °C. The water baths were allowed to warm to temperature and then the pumps were engaged. Measurements were started when the temperature reached the set value after switching on the pumps. At higher temperatures, the deviation from the set temperature is greater because of thermal losses to the system. A temperature of 27 °C was selected for casting because of the cloud point results highlighted in Chapters 3, 4 and 5. Holding the bed at a temperature below the cloud point will induce gelation of the lacquer and the process will thus be driven by a thermal effect. At 27 °C, thermal loss is not an issue for the TIPS–air casting method.

For stability measurements at 35 and 45 °C, an increase in temperature over time from approximately 32 and 40 °C, respectively, was observed for the aluminium spacers. This can be attributed to the lack of any direct heating, with only the two flanking liquid heating plates driving the temperature of the spacers. However, no such increase over time was observed for stability measurements at 25 °C. Thus, it was only at 35 and 45 °C that there was a difference in temperature between the spacers and the rest of the bed, confirming the suitability of 27 °C as the casting temperature for this set-up.

A



B



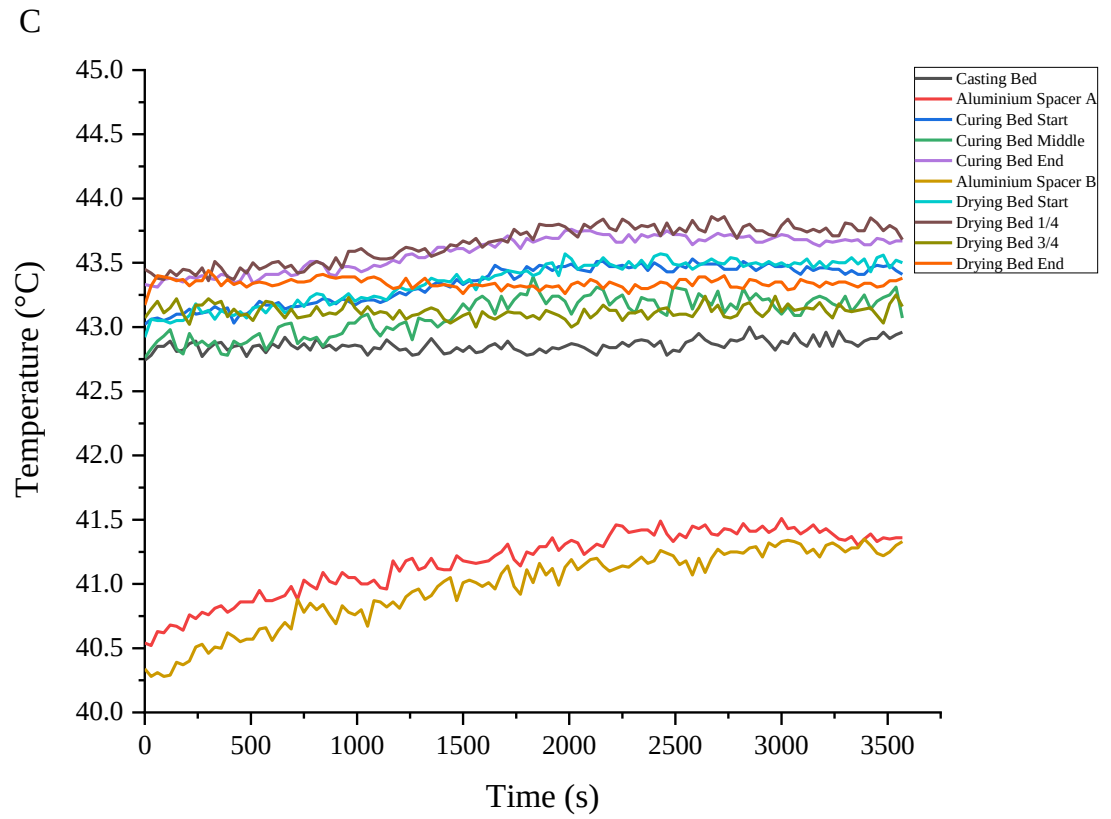


Figure 2.5: Temperature stability over time at various measurement points along the air casting rig for set temperatures of (A) 25 °C, (B) 35 °C, and (C) 45 °C.

2.3 Air delivery system

A set of chambers was built to enclose the heating bed and casting assembly. This allowed the air input to be controlled. Humid air entering the chambers had to be minimised to mitigate any VIPS that could occur if membranes were allowed to cure in untreated air. A desiccant air supply was identified as the most viable approach to achieve this. A Kaiser AIRCENTER SX3 compressor (**Figure 2.6A**) was used as a suitable device for this application. The air flow rate was controlled using an Omega FL-2064 acrylic flow controller (**Figure 2.6C**). The air was heated by passing it through an air heater jet (Radionics RS 860-7198; **Figure 2.6B**). The temperature was controlled using a proportional–integral–derivative (PID) controller, and a resistance temperature detector (RTD) probe mounted on the underside of a baffle controlled the direction of the air entering the curing and drying chambers (**Figure 2.7**).

One of the aims of the study was to investigate the effect of humidity on TIPS–air casting of PMMA membranes. For cost reasons, it was not possible to set precise relative humidity targets for the chambers. Instead, the aim was to achieve low, medium, and high humidity levels according to the equipment available for membrane comparison purposes. Air can be humidified by passing it through a bubbler system comprising a sparging head immersed in water contained in a Duran jar (**Figure 2.6D**). The Duran jar and water are heated on a hotplate to allow control of the humidity as the air temperature in the chambers is heated. **Figure 2.8** shows schematics for different system configurations to achieve low, medium, and high humidity conditions. The humidity was measured using Easylog EL-21CFR-LCD sensors (**Figure 2.9**).

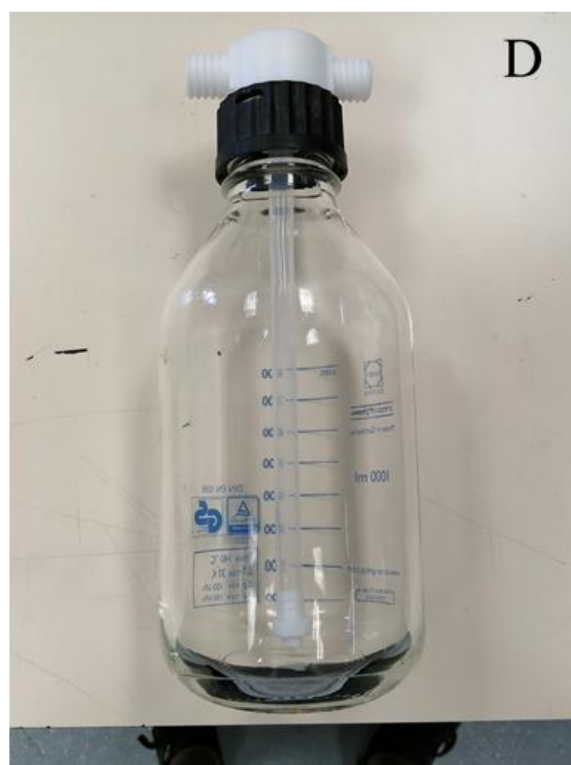


Figure 2.6: Images of (A) the Kaeser AIRCENTER SX3 compressor, (B) heater jets, (C) flow controller, and (D) sparging head on a Duran jar.

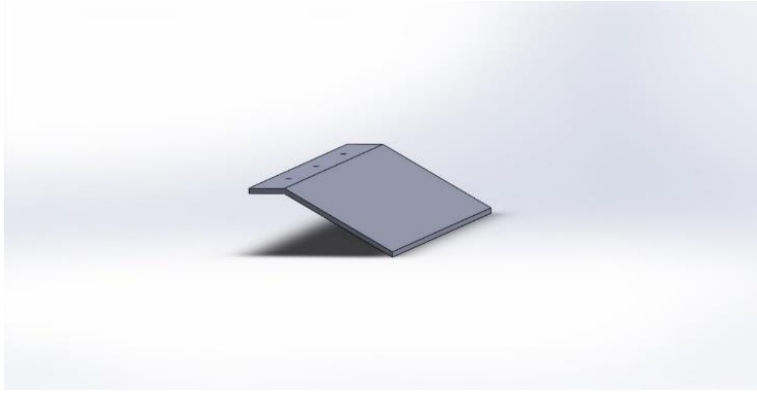


Figure 2.7: Baffle for controlling the air flow direction.

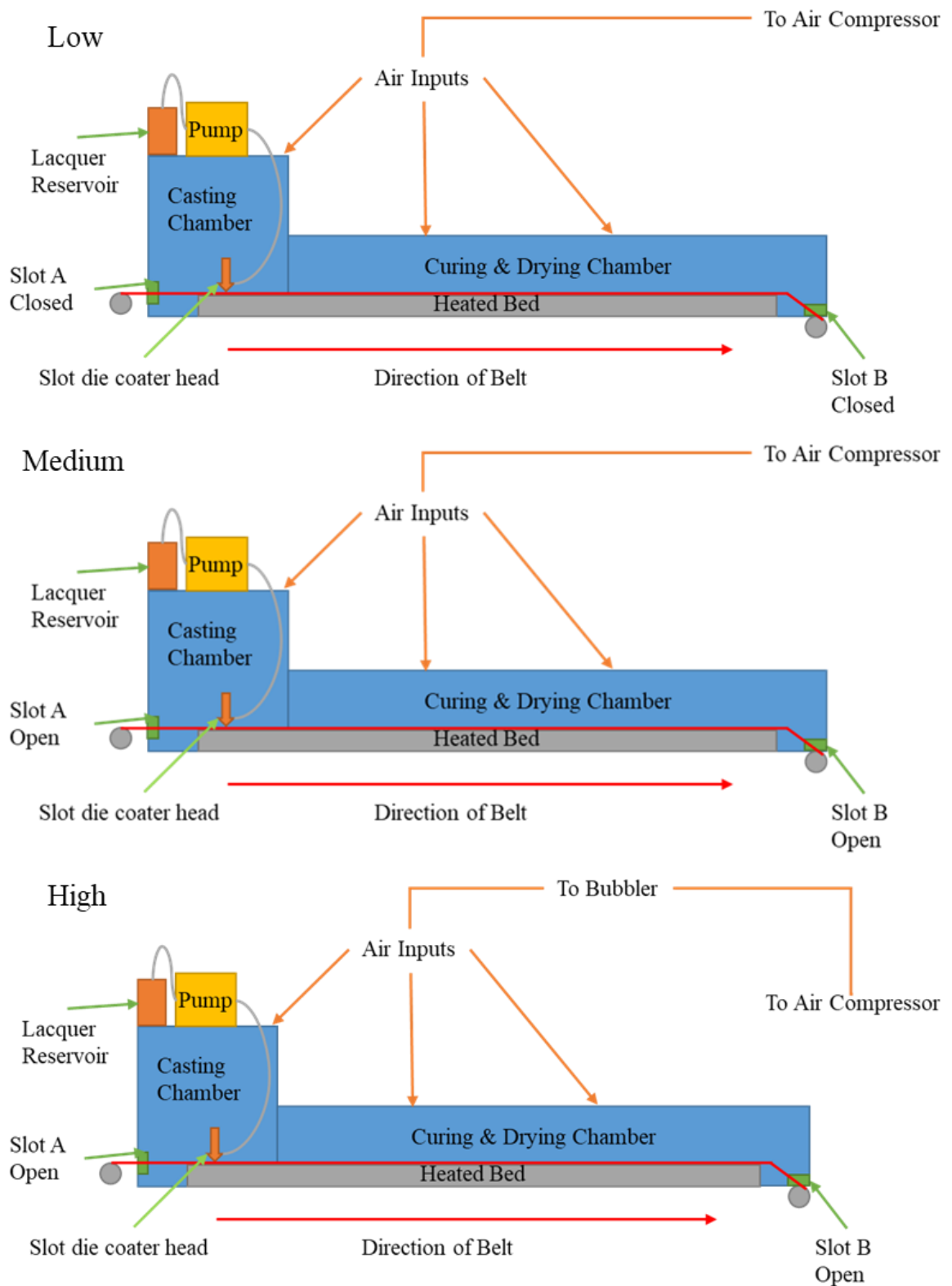


Figure 2.8: Configurations for the air input system for low, medium, and high humidity conditions.



Figure 2.9: Sensor used to monitor air humidity.

The plumbing for the air delivery system is outlined in the schematic shown in **Figure 2.10**.

It consists of a hosing line and appropriate joints, so air is diverted into the three chambers.

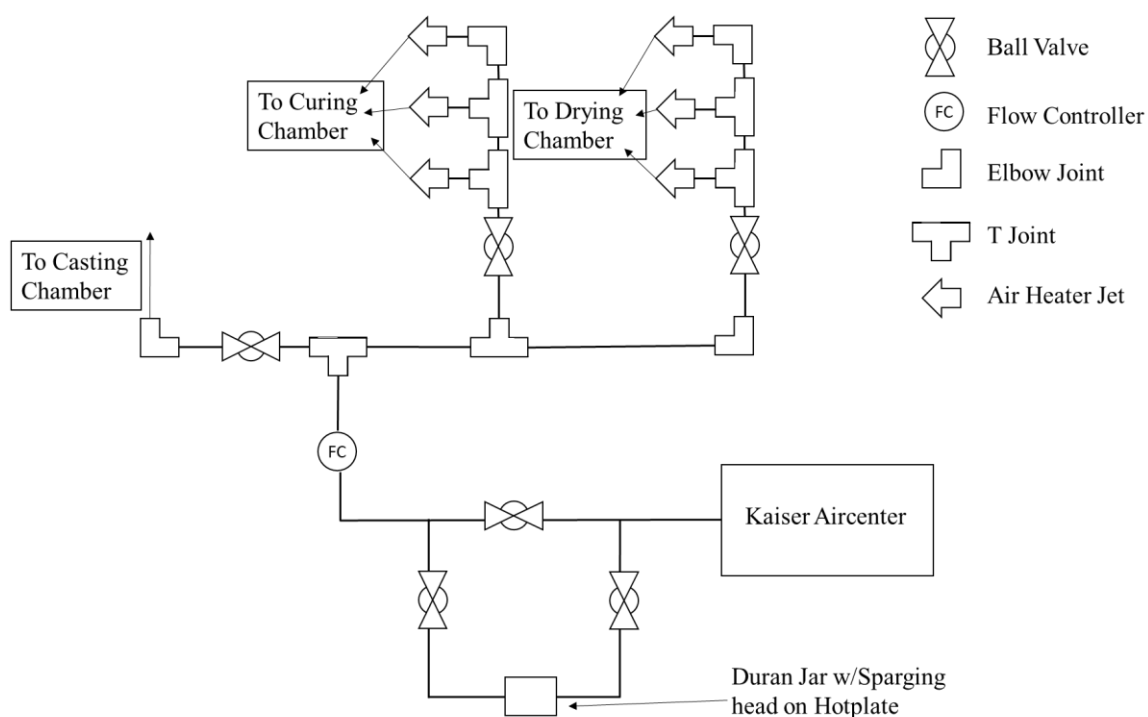


Figure 2.10: Diagram of the tubing for the air delivery system.

Each line has a valve before chamber entry. This allows air to be delivered exclusively to one chamber so that various configurations can be used when curing membranes.

Figure 2.11 shows the circuit for the air jets used to heat the air delivered to the chambers.

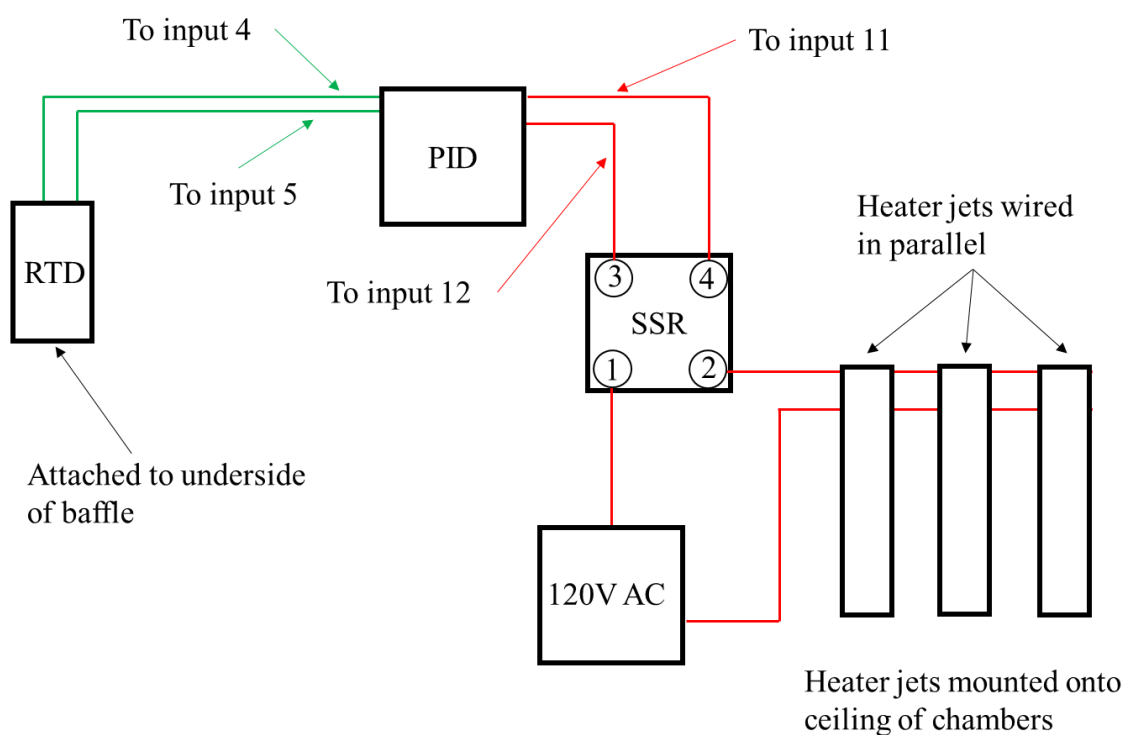


Figure 2.11: PID-RTD circuit for control of the air heaters.

The PID controller is used to maintain the temperature of the air delivered to each chamber at a target value.

Ensuring the airflow is laminar and not turbulent is key to conducting appropriate air changes so that the solvent is removed for efficient phase separation and membrane casting. Turbulent airflow will fail to efficiently remove solvent, as it can often remain in the enclosed chambers due to a swirling effect, as shown in **Figure 1.12**. This effect can limit the evaporation of solvent from curing membranes, as the air delivered to the system will become saturated with vapour over time. Therefore, it is crucial to remove the solvent as rapidly as possible so the evaporation rate does not decrease.

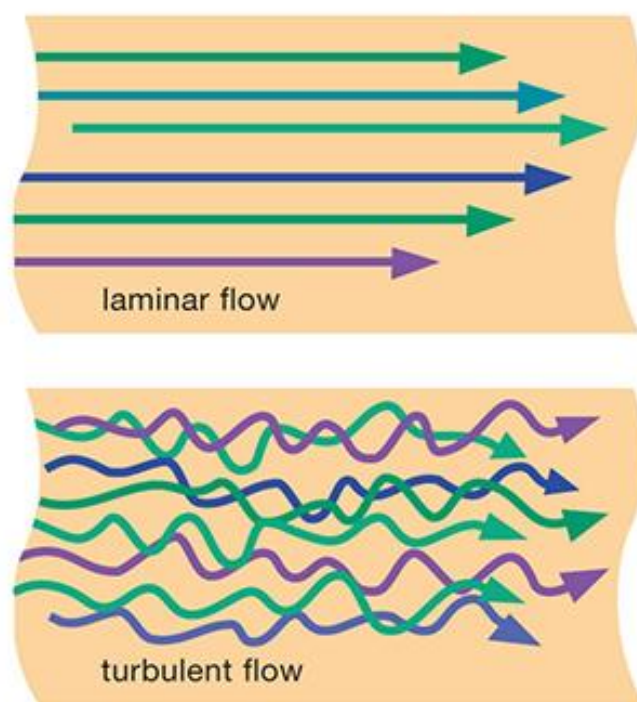


Figure 2.12 Laminar flow versus turbulent flow[3].

Airflow through the chambers was tested by placing lit incense sticks in each chamber and turning the air supply on. A further incense stick was placed at the entrance slot to determine whether there was a slight vacuum effect from the rapidly moving air. **Figure 2.13** shows the configurations that were tested. The absence of an airflow through the casting chamber drew ambient air in through the exit slot, as verified by smoke flowing into the chambers from outside the entry slot. In addition, the presence of a fan to drive solvent and air out of the chambers in combination with the exit baffle caused turbulent air flow. After removing the exit baffles and sealing the exhaust, a more laminar flow was observed (**Figure 2.13C**).

Figure 2.14A shows the air flow when the entry slot was left open: a slight vacuum was still observed. To address this issue, the entrance slot was sealed with a strip of Melinex cut to size and affixed to the panelling. After this modification, smoke from the incense stick flowed towards the drying chamber end of the apparatus and travelled in a laminar manner (**Figure 2.14B**).

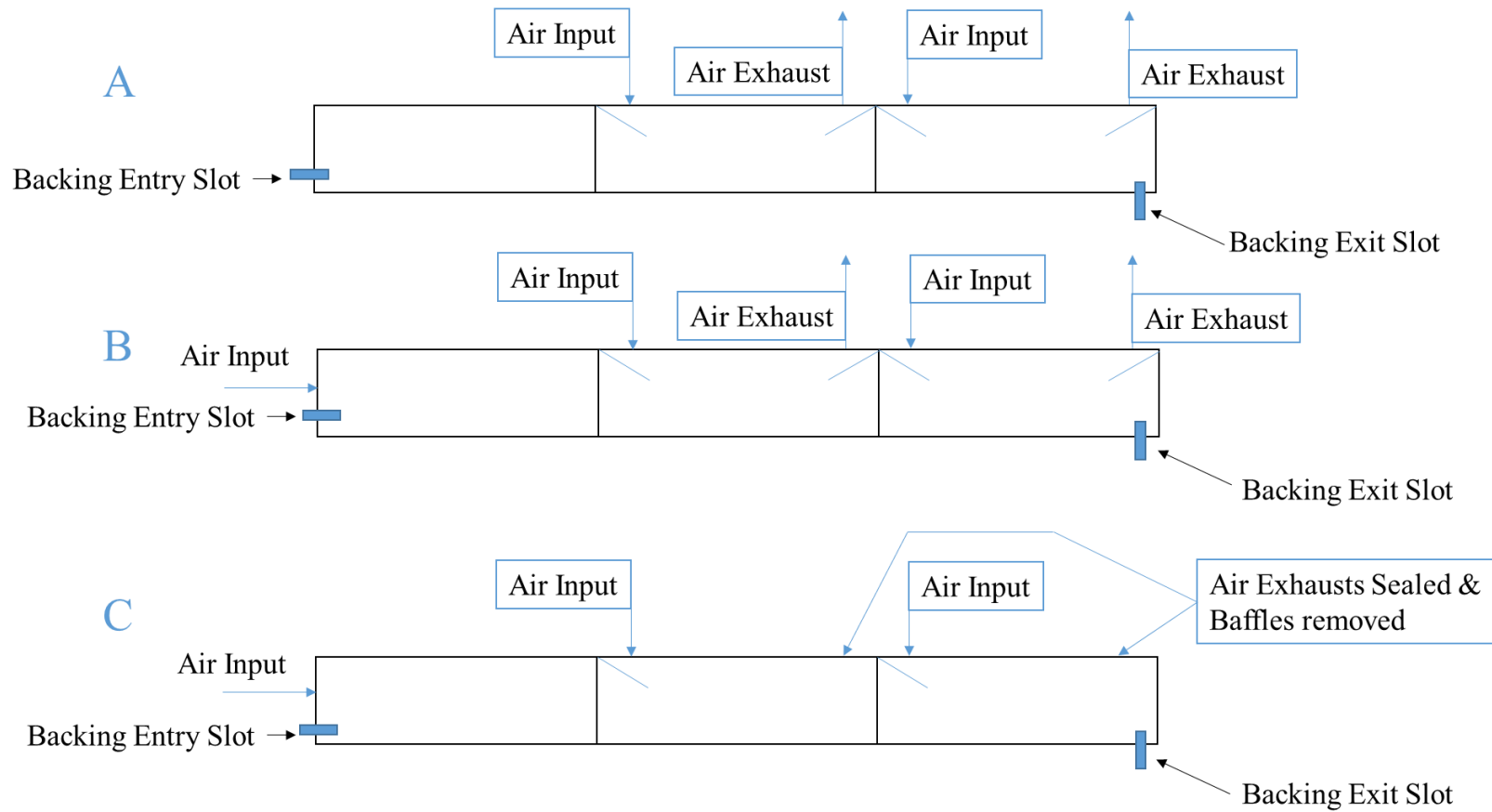


Figure 2.13: Air inputs and exhaust in the air casting rig: (A) original set-up; (B) first revision, with an air input added to the first chamber; and (C) final revision, with air exhausts removed.

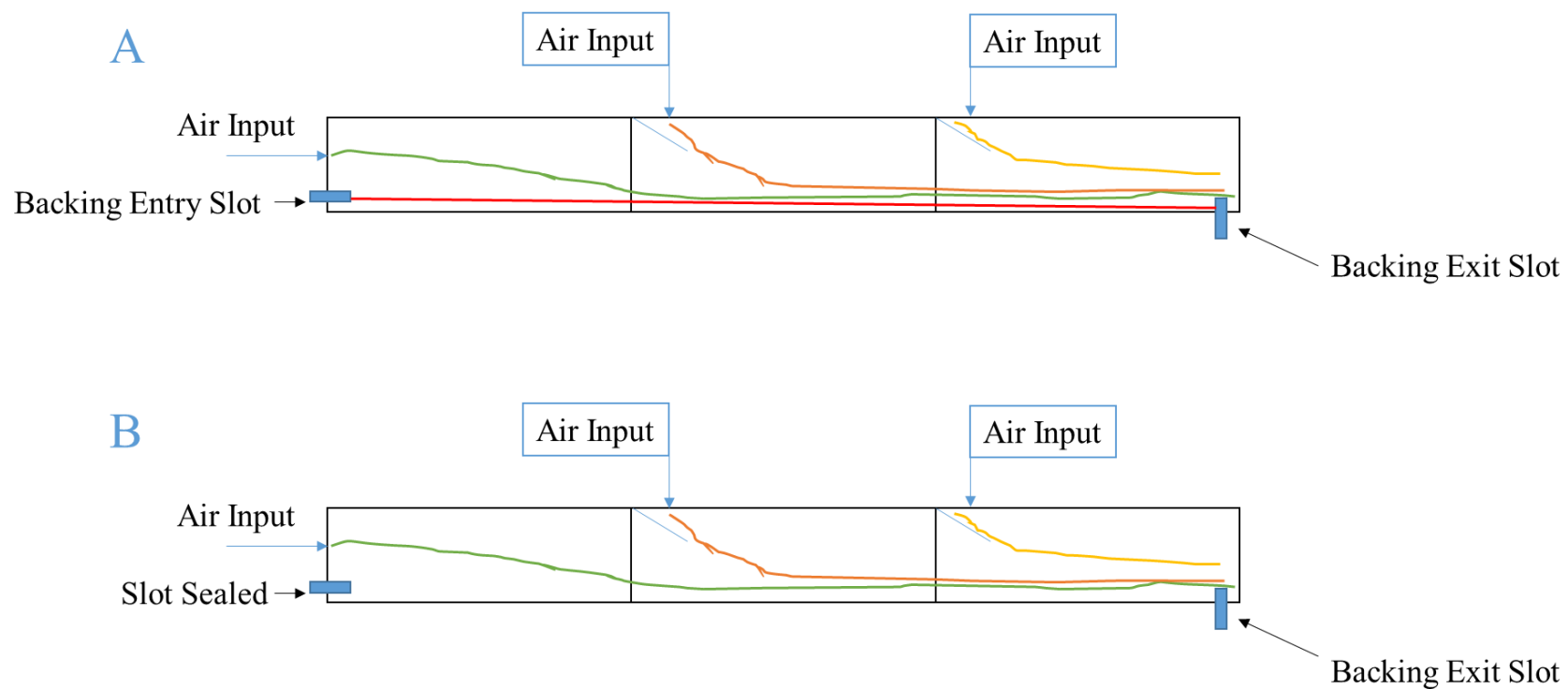


Figure 2.14: Air movement within chambers as tested with incense sticks: (A) original set-up with the backing entry slot open and (B) final set-up with the backing entry slot sealed during curing.

Figure 2.15 shows the circuit used to control the temperature of the air jet heaters mounted in the ceiling of the curing and drying chamber. No heater jets were installed in the casting chamber as the lacquer spends little time in this chamber following deposition.

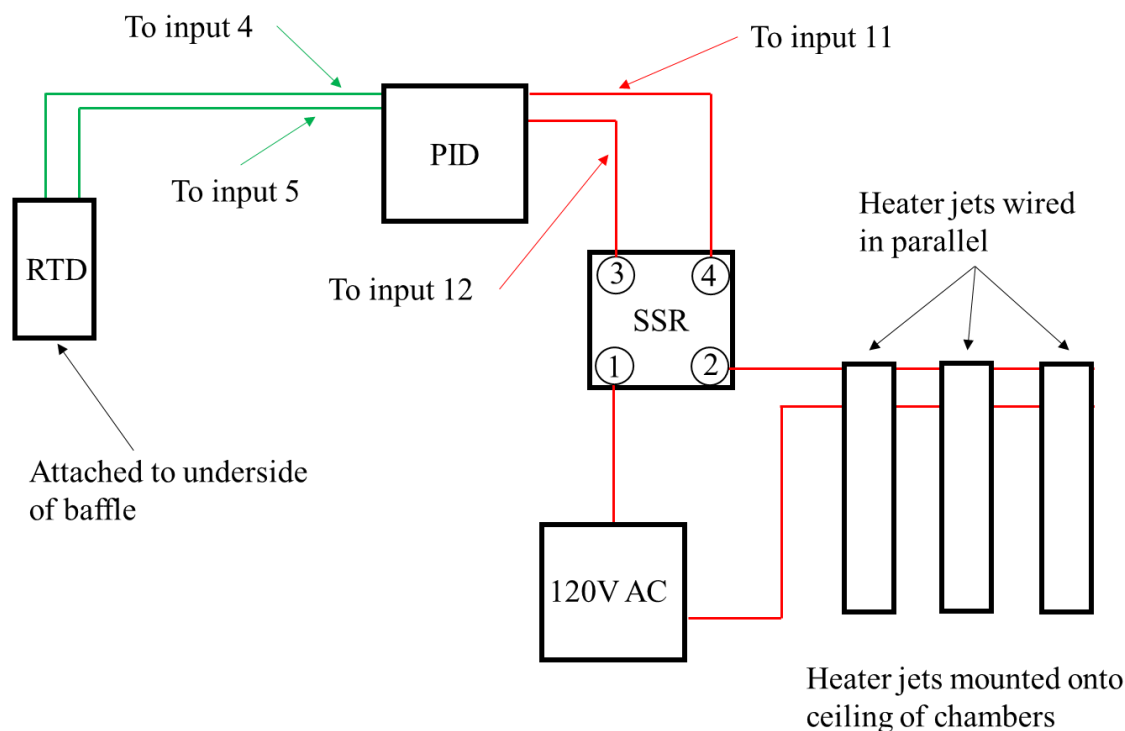


Figure 2.15: Circuit diagram for the air heater jets.

The heater jets were positioned at even intervals in the roof of the curing and drying chambers and the RTD probe was affixed to the base of the baffle. The baffle was constructed from aluminium as its specific heat capacity is quite low and close to that of air (0.9 and $1.0035 \text{ J g}^{-1} \text{ K}^{-1}$, respectively). This allowed measurement of any change in temperature in real time, with feedback from the RTD probe to the PID, which in turn closed the circuit via the solid-state relay (SSR). In this way, the air temperature could be maintained at a set constant value.

Figure 2.16 shows a plot of air temperature with respect to time. The air temperature capabilities of the air jet heaters were tested by setting an initial target temperature of 25°C on the PID controllers and measuring the air temperature within the chambers every 30 s for

a 10-min period. The target temperature was then increased in 10 °C increments and the time taken to reach the new temperature and the temperature stability were measured over the range from 25 to 95 °C).

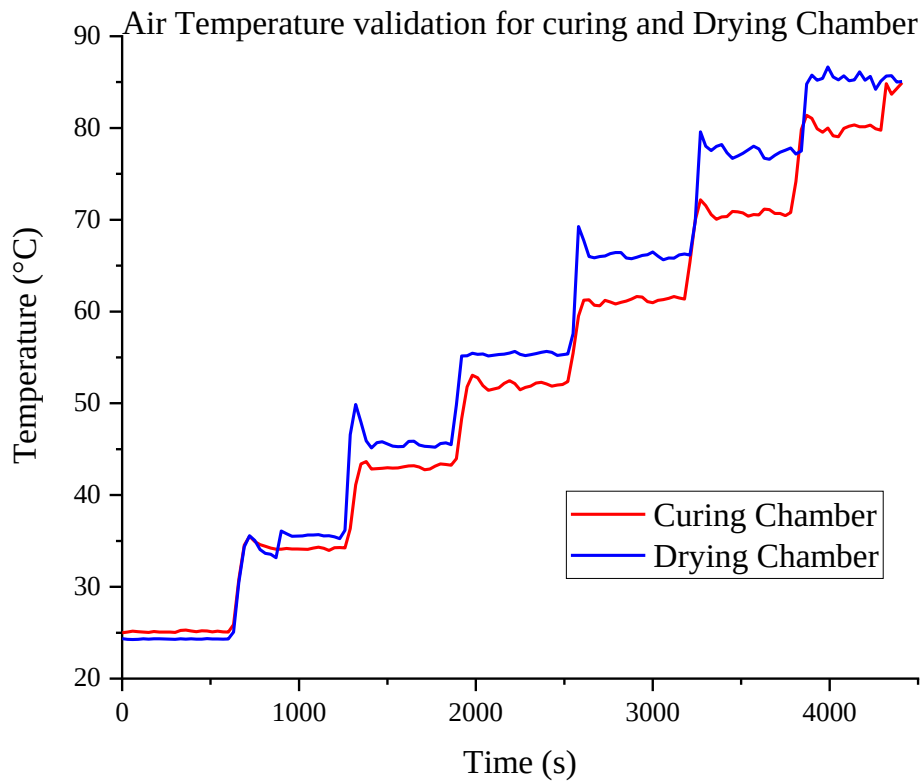
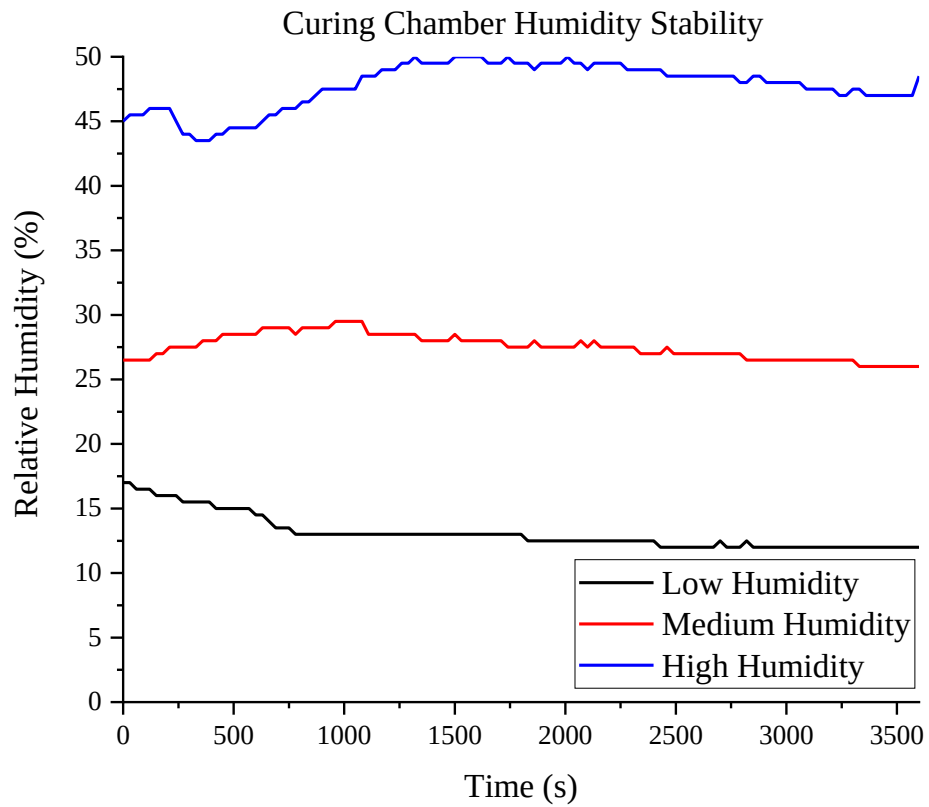
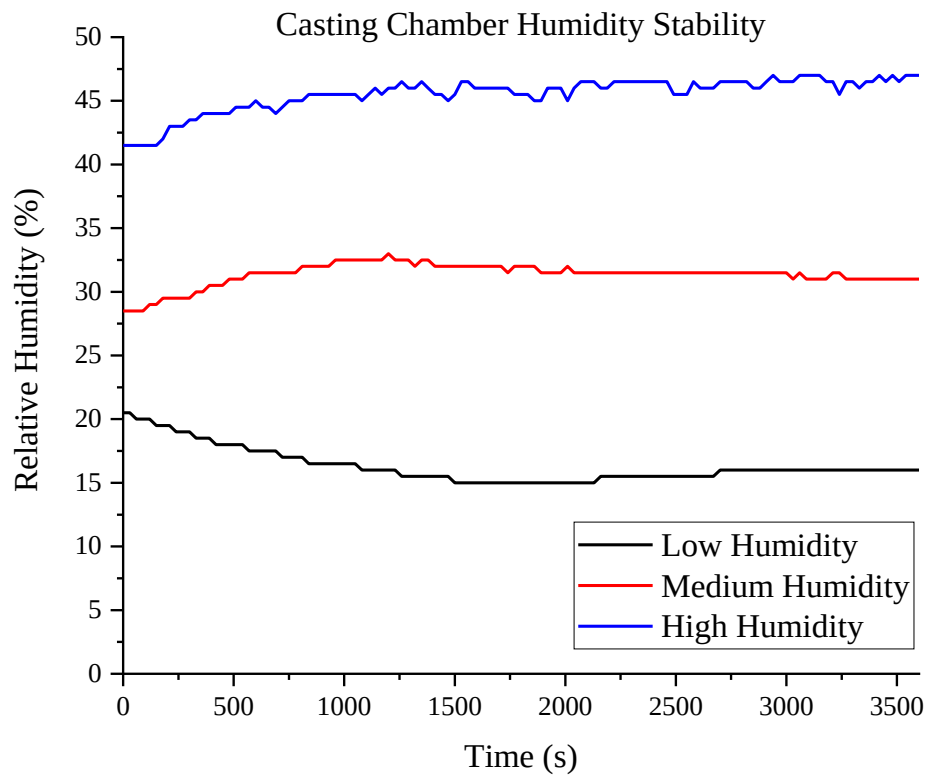


Figure 2.16: Plot of air temperature with respect to time.

It is evident from the data that the air temperature was relatively stable upon reaching the target. However, there was a noticeable overshoot above the target temperature for 45, 65, 75, and 85 °C. This is probably because the thermal conductivity is greater than thermal loss from the system, and the phenomenon was more pronounced at 45 and 65 °C than at 75 and 85 °C. This was not thought to be an issue as the temperature settled at a stable value within 30 – 60 s, and the ~5 °C variation should have no negative impact on membrane integrity.

Figure 2.17 shows validation plots for desiccant, mixed, and humidified air. Humidity was logged at 30-s intervals for a total of 3600 s. A humidity logger (**Figure 2.9**) was first placed

in the middle of the chamber and the dessicant, mixed, or humidified air supply was then switched on. This allowed measurement of the ambient humidity, the time to reach the desired humidity range (low, medium, or high), and the humidity stability up to 3600s.



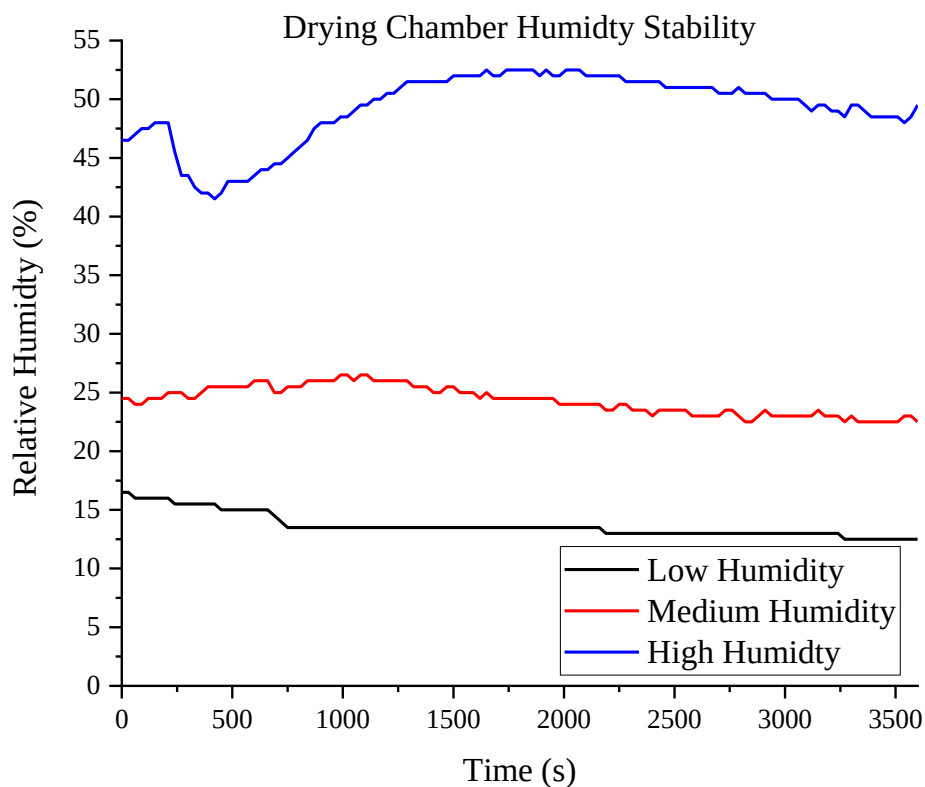


Figure 2.17: Plots of humidity over time for the casting, curing, and drying chambers.

The data in **Figure 2.17** show that when operating at low humidity, the relative humidity first decreased from the ambient level to the target range and then remained relatively stable up to 3600 s, with only slight variations of 1 – 2% in magnitude. For the casting chamber there was a slight increase in humidity after 2100 s. This is because the casting chamber has a greater overall volume and so the volume of air required to maintain constant humidity is greater than that for the curing and drying chambers. However, as the residence time in the casting chamber is less than 10 s, this should have little influence on the membranes produced.

For medium humidity, it took approximately 1000 s for the ambient humidity to increase to the target range and stabilise. The variation over time thereafter was greatest for the curing and drying chambers, but this variation was no greater than 5%, which is acceptable precision for determining the effect of humidity on membrane fabrication. These greater

humidity variations than for the casting chamber can be attributed to the air movements in the chambers noted during testing (**Figure 2.14**). Mixing of air as it travels from the casting chamber through the curing chamber and on to the drying chamber leads to slight changes in humidity.

At high humidity the target humidity range was reached at approximately 1250 s. Variations in humidity thereafter for the curing and drying chambers are again most likely due to the air mixing observed during testing (**Figure 2.14**). The more pronounced drop in humidity observed in the drying chamber can probably be attributed to the exit slot being left open, exposing this chamber to a further area from which ambient air can mix and enter the chamber.

While some variation in relative humidity was observed, overall, the stability results show that the humidity can be controlled to an acceptable range for determining the effect of humidity on phase separation and membrane production. This confirms that the cost-effective approach taken for humidity was suitable for experimental membrane production. In addition, the control over air volume and temperature allowed the development and refinement of an air casting process.

2.4 Slot coater assembly

The slot coater is a crucial component of the air casting apparatus and allows controlled delivery of the casting solution onto the casting bed. It comprises a series of stainless steel plates with an array of metal spacers that define the area into which the casting solution is pumped, which subsequently defines the area on the casting bed onto which the casting solution is extruded. **Figure 2.17** shows the main components of the slot coater.

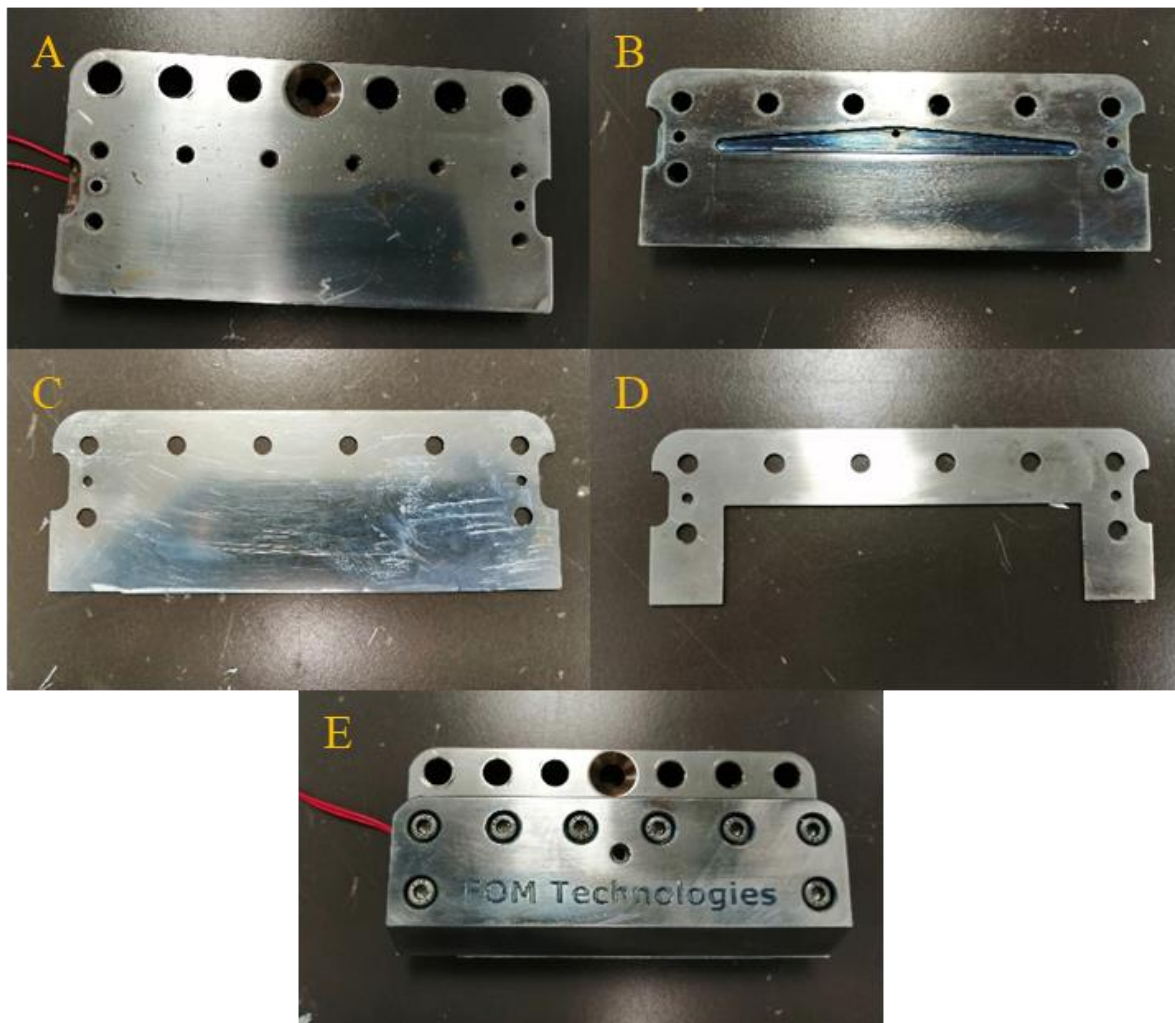


Figure 2.18: Slot coater components: (A) back plate; (B) front plate; (C) backing spacer sheet; and (D) spacer sheet. (E) Fully assembled slot coater.

The slot coater comprises two metal plates: a backing plate with a smooth surface (**Figure 2.18A**) and a face plate with a small reservoir and a hole through which lacquer can be delivered (**Figure 2.18B**). In addition, there is a backing shim to ensure a smooth surface

when lacquer is pumped through the face plate (**Figure 2.18C**) and a slotted shim that defines the area into which the lacquer is pumped (**Figure 2.18D**). The area into which the lacquer is pumped is measured 10 cm × 2.5 cm. Shims of width 100 µm (×2), 200 µm (×2), and 1 mm were supplied with the slot coater.

Assembly of the slot coater is shown in **Figure 2.19**. The steps for assembly are as follows:

1. First the base plate is placed facing up and the backing shim is aligned with the screw holes.
2. Slotted shims of desired width are placed on top of the backing shim and aligned with the screw holes.
3. The face plate is placed on top of the shims and aligned with the screw holes.
4. The top outermost screws are finger tightened, followed by the lower screws.
5. The centre top screws are finger tightened.
6. The remaining screws are finger tightened.
7. The screws are tightened with an Allen key in the order above until there is no movement.
8. The slot coater is mounted on the stand in the casting chamber.
9. The power cable for the silicone heater is connected.

After each casting run it is important to disassemble and clean the slot coater with isopropyl alcohol to remove any residual solvent and polymer from the slot.

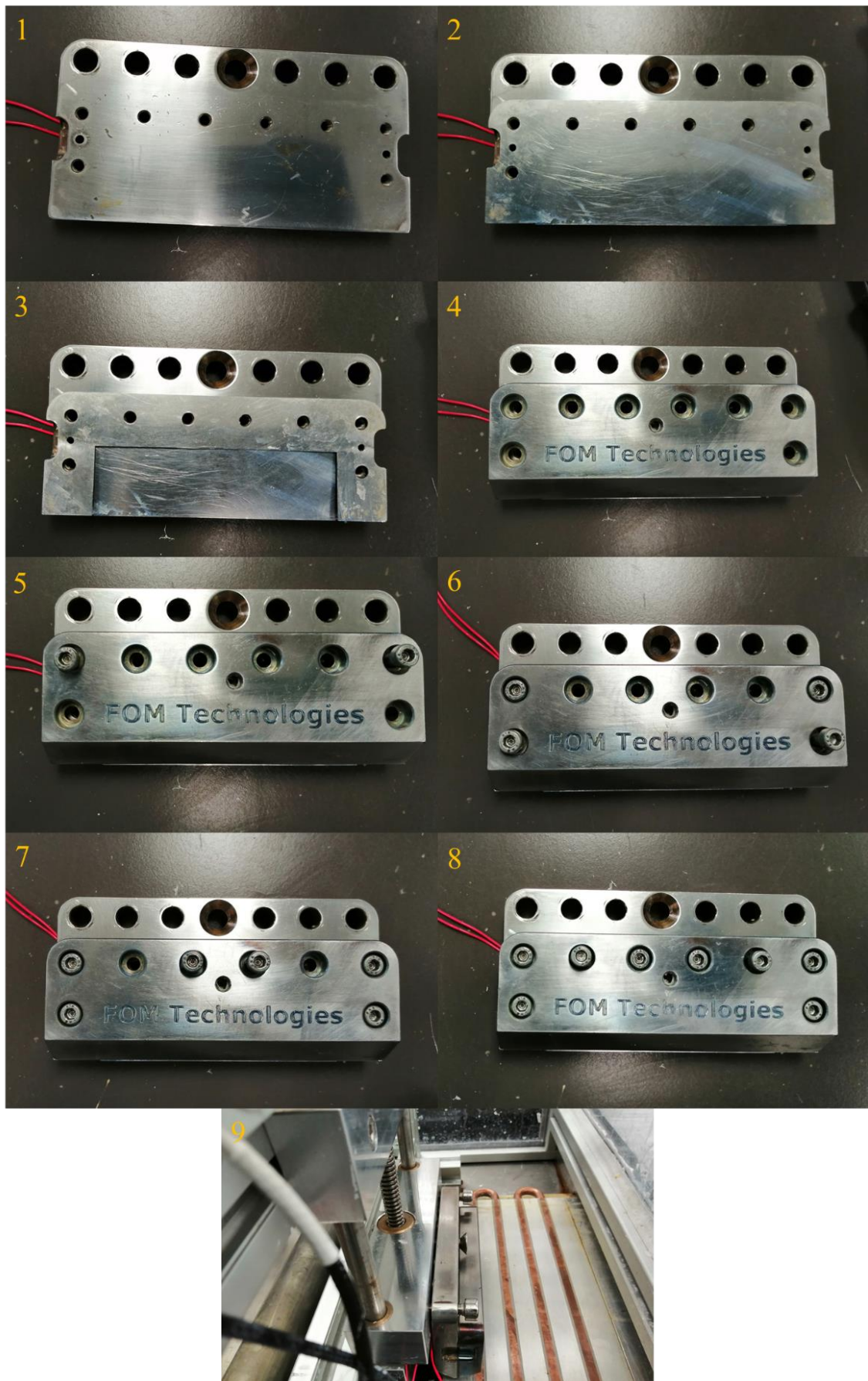


Figure 2.19: Stepwise assembly of the slot coater.

Figure 2.19 shows the circuit for control of the slot coater temperature.

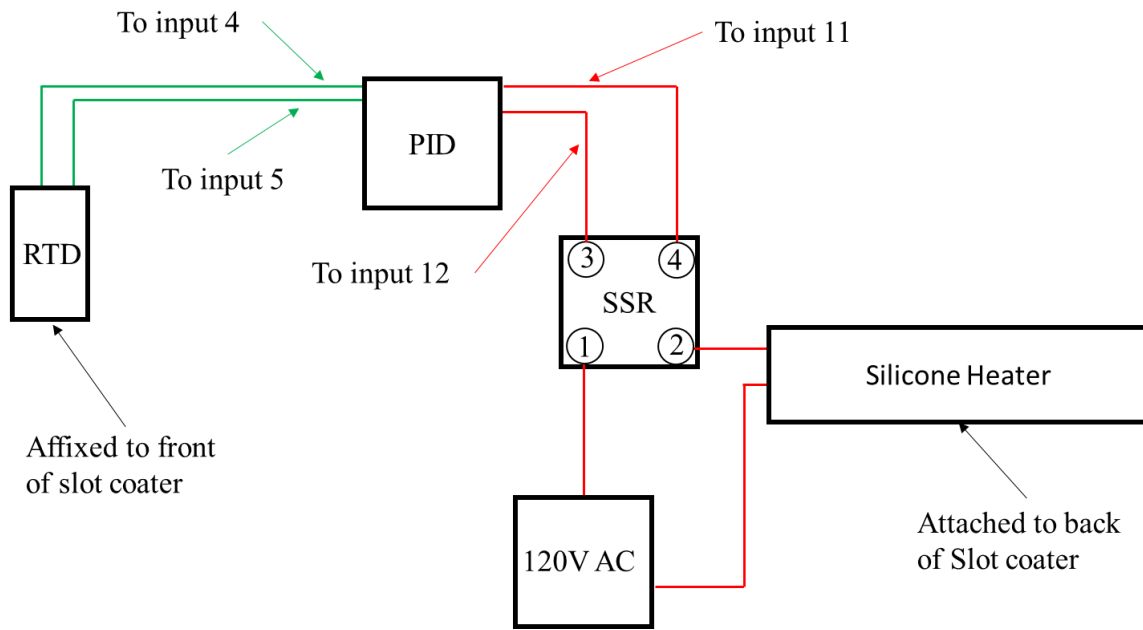


Figure 2.20: Circuit diagram for the silicone heater mounted on the slot coater.

The RTD affixed to the front of the slot coater is used to keep its temperature constant. Similar to the air temperature, if the RTD probe senses a change in temperature, the switch in the SSR is closed and the heater is switched on. This results in a constant temperature that is set above the cloud point temperature of the lacquer in use, and thus allows controlled phase separation on the casting bed as opposed to in the slot coater.

2.5 Full apparatus

Figure 2.21 shows the fully assembled apparatus.

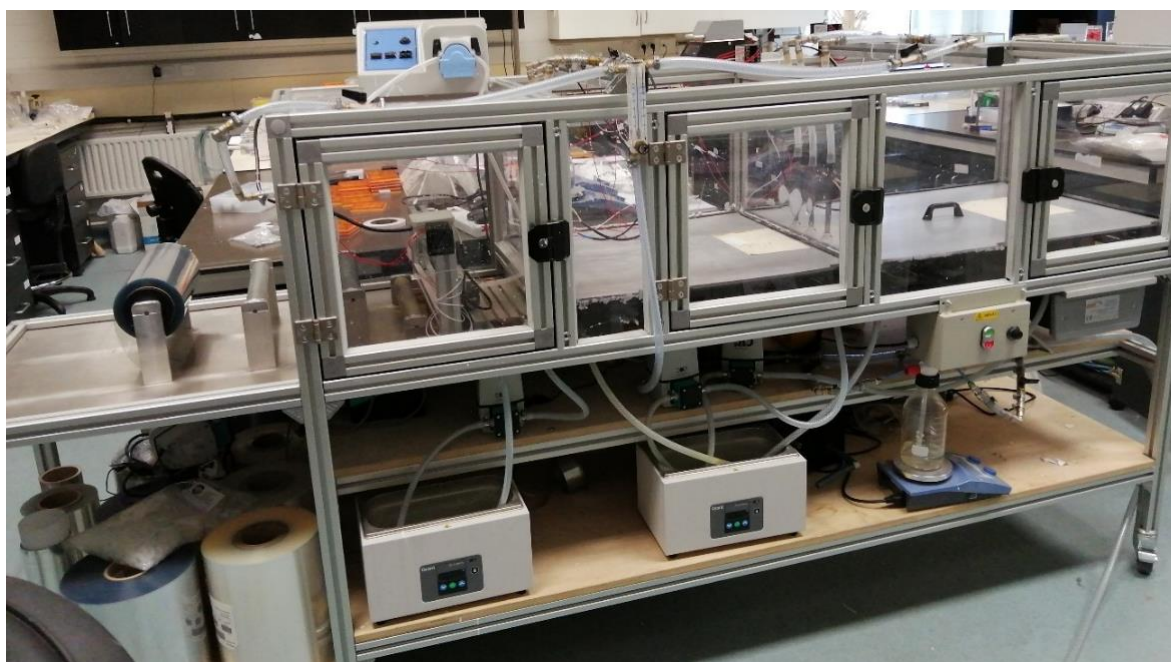


Figure 2.21: Final air casting apparatus. Photograph of the fully assembled apparatus in the laboratory.

The qualification data presented here and the data in Chapters 3, 4, and 5 confirm that the air casting apparatus developed is suitable for experimental fabrication of membranes. However, it is limited to experimental work only and any attempts to scale up the membrane production processes would require a more robust setup with more precise control over the various components and operating parameters.

2.6 Conclusion

The apparatus constructed is capable of casting PMMA membranes. However, several issues were noted after construction that could easily be remedied with upgrades:

- **Use of glass for chamber construction.** The polycarbonate panelling used for the chamber walls could be replaced with glass. When operating at higher temperature ($>90\text{ }^{\circ}\text{C}$) warping of the panelling was observed due to excessive heat generated by the heater jets. Installation of boronated glass would overcome this issue and allow the use of higher temperatures.
- **Use of heated piping to minimise premature phase separation of the lacquer.** The plastic/rubber hosing could be replaced with heated metal piping. When operating the apparatus with the bubble engaged, a significant amount of water was observed in the lines because of the temperature difference between the Duran jar and the lines delivering air to the chambers. The presence of water in the lines suggests the occurrence of phase separation because the tubing temperature is below the dew point of the humidified air. Heating of the tubing would prevent phase separation and could allow the air delivered to the chamber to exceed the maximum humidity achieved of $\sim 52\%$.
- **More precise control of air flow and volumes.** The shutoff valves could be replaced with a flow controller so that the air volumes in each chamber could be measured and set. This would be useful and provide further data on air change rates at each stage. The air change rate can be calculated from the air flow rate and the volume of the chambers. This information would be especially useful for future scale-up of casting runs.
- **Separate chambers around the Melinex mount and the motor wind up.** As humidity needs to be tightly controlled when running the apparatus, addition of new

chambers around the support mount and the motor would further reduce entry of unconditioned air into the system and minimise potential changes in humidity.

- **Piston-style pump for lacquer delivery to the slot coater.** Adding a piston-style pump instead of a peristaltic pump would allow more even pressure when pumping the lacquer into the slot coater. The back pressure generated from the back plate and the confined space into which lacquer is pumped can limit the amount of lacquer delivered to the belt. This could be overcome by placing more spacers in the slot coater to increase the slot width, which would in turn reduce the back pressure.
- **Attenuated motor speed for continuous operation.** For continuous process operation, the motor could be replaced with a slower one; alternatively, a gear train could be used to slow down the existing motor. This could allow the apparatus to run in a continuous mode and the viability of any processes being run in a continuous manner could then be determined. However, further upgrades such as the piston pump mentioned previously and heated lines for air would need to be implemented. In addition, the lacquer would need to be heated for the duration of the process, as well as the line connecting the lacquer reservoir and the slot coater.
- **Greater control of the heated bed.** The heated bed could be replaced with a fully electric bed equipped with a PID controller similar to the set-up used for controlling the slot coater and air temperature. However, such a system would be cumbersome and would need multiple inputs at various points along the bed and thus would be very costly.

While the above upgrades could be implemented, the existing apparatus is suitable for casting membranes and monitoring the important parameters associated with air casting: the air humidity, air temperature, and bed temperature. The suggested upgrades would be more suitable for process optimisation before commercial manufacture or use.

References

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Chapter 3

Development of an Air casting–TIPS Method

Abstract

This chapter describes the development of a reproducible method for air casting of PMMA membranes via the TIPS method using the nonsolvent-induced phase separation variation. Membranes were fabricated using a custom-made apparatus that allows control of the humidity, air flow rate, and casting bed temperature.

By controlling these variables, highly porous PMMA membranes were formed at various concentrations. Studies were conducted on the polymer–solvent lacquer blend to determine the phase separation characteristics and the shelf life as a function of the PMMA concentration. The results show that the lacquer cloud point is inversely proportional to the PMMA concentration and that the combination of TIPS and air casting can yield membranes with various pore volumes and pore sizes ranging from 0.91 to 1.81 μm . Skinning increased with increasing PMMA concentration, with skin coverage ranging from 4.4% to 100% over various samples. CFT was also affected by the PMMA concentration, with times ranging from 217 to 517 s depending on the concentration. The differences in CFT by PMMA concentration were statistically significant.

3.1 Introduction

The design of a repeatable, reliable, consistent and robust process that combines air casting and thermally induced phase separation of components is the focus of this study. Ideally, the aim is to develop a lacquer that on casting can be thermally triggered so that the concentration crosses a phase line between polymer solubility and insolubility. The solvent present at the phase line acts as the porogen. Several factors contribute to the viability of combining the two techniques. First, the composition of the casting solution is critical in the development of a robust method. The casting solution needs to be stable so that a highly swollen gel (as this will yield a highly porous structure on drying) will precipitate when its temperature is decreased. In the case of PMMA, it has been shown that the polymer can swell in low-molecular-weight alcohols [1]. Ethanol is a suitable alcohol and butanol is an ideal ‘trigger’ as it switches from a solvent to a non-solvent around room temperature. These methods have previously been utilised for the fabrication of PVDF hollow-fibre membranes [2,3]. Acetone is a well-known solvent for PMMA and is miscible with alcohols. This is a good choice of solvent as it has high volatility for rapid precipitation and results in swift formation of the alcohol swollen PMMA gel phase. Thus, a combination of acetone, ethanol, and butanol provides the ideal mix of solvent and non-solvents for the air casting technique [4,5], as PMMA will freely dissolve in acetone but is only partially soluble in both ethanol and butanol, allowing phase separation to occur as the temperature is altered and acetone is removed via evaporation.

Since the separation is triggered by a thermal process (largely the change in PMMA solubility in butanol), the stability of the casting solution or lacquer is critical. To determine the stability and characteristics of casting solutions, it is necessary to determine their behaviour as a function of temperature. This can be achieved by measuring the turbidity of the solution over a set temperature range, from which the cloud point and by extension the

gelation point can be determined. Identification of the cloud point can help in designing a more robust process and in determining appropriate temperatures for the air supply during the membrane curing process.

Following lacquer characterisation, the process parameters can be more closely examined, as Aoutlined in Chapter 2. The apparatus designed for these experiments allows variation of a number of critical parameters, including the belt temperature, air temperature, and curing time. By varying these parameters, it should be possible to produce membranes with different properties.

3.2 Materials and methods

3.2.1 Materials

PMMA was obtained from Arkema (Altuglas[®] BS572). Acetone (HPLC grade, $\geq 99.5\%$) was purchased from Honeywell, butanol (HPLC grade, $\geq 99.7\%$) was purchased from Sigma Aldrich, and ethanol (HPLC grade, $\geq 99.9\%$) was purchased from Fischer Scientific. Polyester backing (Melinex 401, 75 μm in thickness) with a slip agent coated surface on one side was purchased from Teijin Films. The slip agent is unknown due to commercial sensitivity. Sodium dodecylbenzene sulfonate (SDBS, technical grade) and THF (spectroscopic grade) was purchased from Sigma Aldrich.

3.2.2 Molecular weight analysis of PMMA

The average molecular weight (M_w), molecular number (M_n), and polydispersity index (PDI) of PMMA were measured using a Viscotek TDAmx gel permeation chromatography (GPC) system (Malvern Panalytical) consisting of 80-mm analytical columns of porous styrene divinylbenzene copolymer gel coupled to a triple-detector array (TDA) comprising refractive index, viscometer, and light scattering detectors. Spectroscopic grade tetrahydrofuran (THF) was used as the eluent at a flow rate of 1.0 mL min^{-1} . The sample injection volume was 100 μL . Samples were prepared in THF at a concentration of 0.1% (w/v) and stirred for 24 h at room temperature to ensure complete dissolution and homogeneity. Dissolved samples were loaded into an autosampler maintained at 35°C to prevent the samples from precipitating out of solution. A molecular weight calibration curve was generated using two PMMA standards of known molecular weight (95 kDa and 350 kDa). The chromatograms acquired for all the samples were processed using the Viscotek

OmniSEC software for homopolymers. Each sample was run twice, with two injections for each run, and the mean results were calculated.

3.2.3 Pre-drying of PMMA

Weighing boats were placed on a KERN ABJ320-4NM analytical balance and their mass was noted. The balance was then zeroed and approximately 1 g of PMMA was added and weighed accurately. This was repeated twice more for 1 g samples and three times for samples of 10 g. All the samples were placed in a Memmert UN55 oven held at 60 °C. The samples were removed at 24 h intervals and reweighed, the loss in mass was recorded, and the samples were then returned to the oven. This process was repeated until the mass had stabilised and no further mass loss was observed.

3.2.4 Lacquer formulation with PMMA loading on a percentage basis

Solvent blends were formulated for lacquers containing between 3.5% and 4.5% PMMA using the ratios shown in **Table 3.1**. The butanol and ethanol weights were kept constant and the weight of acetone was varied with the PMMA weight. Solvents were weighed into a 250 mL Duran jar using a Fischer Scientific model PSS6001 analytical balance. After each addition, the balance was set to zero and the lid on the jar was secured. Solvents were added in the order of least to most volatile (butanol, ethanol, acetone). When all three solvents had been added, a magnetic stirring bar (40 mm x 0.5 mm) was added to the jar, which was then sealed and placed on an IKA RET hotplate held at 40 °C, with the magnetic stirrer set to 600 RPM. The solvent mix was stirred for 1 h to ensure homogeneity. Then the applicable amount of PMMA was weighed out using a KERN ABJ320-4NM analytical balance and added to the solvent mix. The polymer–solvent solution was then replaced on the hot plate and allowed to stir at 40 °C at 600 RPM for 24 h before casting.

Table 3.1: Lacquer formulations for PMMA loading on a percentage basis.

Sample ID	Lacquer composition (w/w %)			
	PMMA	Acetone	Butanol	Ethanol
A	3.5	41.3	27.6	27.6
B	3.6	41.2	27.6	27.6
C	3.7	41.1	27.6	27.6
D	3.8	41.0	27.6	27.6
E	3.9	40.9	27.6	27.6
F	4.0	40.8	27.6	27.6
G	4.1	40.7	27.6	27.6
H	4.2	40.6	27.6	27.6
J	4.3	40.5	27.6	27.6
K	4.4	40.4	27.6	27.6
L	4.5	40.3	27.6	27.6

3.2.5 Lacquer formulation with PMMA as a function of mass

Lacquers were also prepared with the formulations shown in **Table 3.2** for which the butanol, ethanol, and acetone weights were kept constant and only the weight of PMMA was varied. Solvents were weighed into a 250 mL Duran jar using a Fischer Scientific model PSS6001 analytical balance. After each addition, the balance was set to zero and the lid on the jar was secured. Solvents were added in the order of least to most volatile (butanol, ethanol, acetone). When all three solvents had been added, a magnetic stirring bar (40 mm $\times$ 0.5 mm) was added to the jar, which was then sealed and placed on an IKA RET hotplate held at 40 °C, with the magnetic stirrer set to 600 RPM. The solvent mix was stirred for 1 h to ensure homogeneity. Then the applicable amount of PMMA was weighed out using a KERN ABJ320-4NM analytical balance and added to the solvent mix. The polymer–solvent solution was then replaced on the hot plate and allowed to stir at 40 °C at 600 RPM for 24 h before casting.

Table 3.2: Lacquer formulations for PMMA loading on a weight basis.

Sample ID	Lacquer composition (g)			
	PMMA	Acetone	Butanol	Ethanol
PMMA 2.5g	2.5	42.4	28.8	28.8
PMMA 5g	5	42.4	28.8	28.8
PMMA 7.5g	7.5	42.4	28.8	28.8
PMMA 10g	10	42.4	28.8	28.8

3.2.6 Membrane fabrication

Membranes were fabricated via an air casting method using the apparatus described in Chapter 2. **Figure 3.1** shows a general schematic and the set-up for supplying desiccant and humidified air streams to the apparatus.

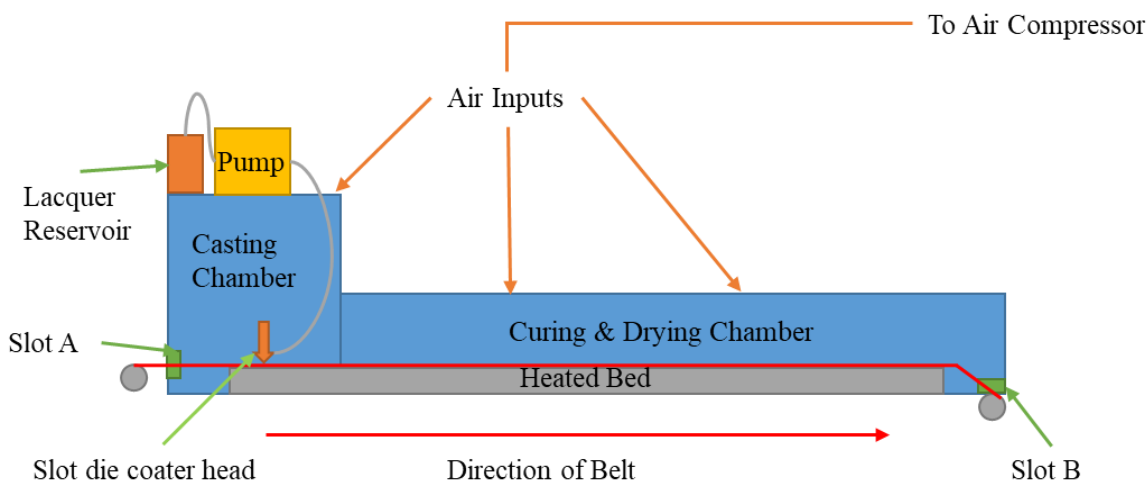


Figure 3.1: Diagram of the apparatus set-up for desiccant air delivery. See text for details.

Desiccant air was supplied by a Kaeser AIRCENTER SX3 compressor and pumped into the casting and curing/drying chambers at a rate of 50 L min^{-1} and pressure of 1 bar before lacquer deposition. The air delivered to the curing and drying chambers was heated to 27°C using a series of heated coils and a proportional–integral–derivative controller to monitor

and control the temperature. The chambers equilibrated for 20 min before lacquer deposition. Immediately before lacquer deposition, the air supply to the casting chamber was closed and the belt and the pump were switched on. The lacquer was then pumped through a slot die-coater head (FOM Technologies) with a spacer width of 200 μm onto a polyester backing drawn across a heated bed held at 27 °C. Following deposition, the polyester backing was cut at either end, and both the entrance and exit slots were sealed (slots A and B in **Figure 3.1**), resulting in relative humidity of 11.5–14%. The membranes were sealed in the curing and drying chamber for 1 h and the air temperature was increased according to the schedule in **Table 3.3**. After 1 h had elapsed the membrane was removed from the chamber, cut into three sections (start, middle, and end of the run) of approximately 30 cm in length, and then placed in a tray containing 1 L of tap water to remove any unevaporated solvents from the membrane matrix.

Table 3.3: Air temperatures and time elapsed during the membrane preparation process.

Air temperature (°C)	Time elapsed (min)
27	0
43	10
41	20
48	30
55	40
60	50

3.3 Characterisation

3.3.1 Lacquer characterisation

Lacquers were characterised by measuring the turbidity using a Lovibond TB 100 tintometer during sample cooling. Aliquots of 10 mL of lacquer were removed from the stock solution and placed in airtight vials, with three vials prepared for each lacquer. Each vial was placed in a water bath at 35 °C and allowed to equilibrate for 10 min. Once at equilibrium, the vial was removed, dried of excess water, and placed in the tintometer. The nephelometric turbidity units (NTU) value was noted, and the vial was replaced. This process was carried out for all three vials and the average of the three was taken as the NTU value for that lacquer at that temperature. This process was repeated until the lacquer became turbid and white in appearance. The data generated were plotted as a graph of turbidity versus temperature to determine the cloud point of each lacquer.

3.3.2 SEM imaging

Samples were imaged using a Zeiss Ultra SEM instrument with a Gemini electron optical column and an acceleration voltage of 2.5 keV. Images were taken of the skin (the open side of the membrane that faces into the air) and belt layers (the closed side of the membrane facing the Melinex) as well as cross-sections of the membrane samples. Skin and belt layers were placed on a stub using a flat-tipped tweezers to prevent damage to the membrane. For the belt layer it was ensured that the membrane was fully detached from the polyester backing. Cross-sections were prepared by cryofracture using liquid nitrogen. Samples were immersed in liquid N₂ and removed when the boiling had ceased, and then fractured to give a clean edge using two sets of tweezers, as described by Flynn et.al [6]. Samples were coated in a thin layer (approx. 10 nm) of gold and palladium using a Cressington 208HR sputter

coater before imaging to prevent charging. Samples were scanned in triplicate and the best resolved images were reported.

3.3.4 Capillary flow time

The capillary flow time is defined as the time taken for a solvent front to move through a piece of the membrane. It is an indicator of the pore structure and surface chemistry. Samples of membrane were cut into strips of 4 cm × 1.5 cm across the web from the middle of the cast run and the centre of the membrane, ensuring that the backing remained on the sample. The strips were placed in a 0.1% w/w solution of SDBS and allowed to wet for 10 min. This surfactant renders the membrane hydrophilic allowing permeation of aqueous solutions. The samples were then removed from the solution and placed on a microscope slide, with the backing side facing the glass, and dried in an oven at 30 °C for up to 1 h to ensure all water was dried from the inside of the membrane. While samples dried, a mantle (**Figure 3.2**) was prepared with 300 µL of eosin dye solution. The air temperature and relative humidity in the room were measured to ensure they fell within the optimal range of 19.5–22.5 °C and 45–55%, respectively, as outlined in a procedure defined by Merck Millipore [7]. If the ambient conditions were outside this range, the samples were not tested to ensure consistency. When samples had completely dried, they were placed in the mantle and the time taken for complete wetting was measured. Samples were tested in triplicate and the capillary flow time (CFT; also called wicking time) was recorded, with results reported as the range and mean.

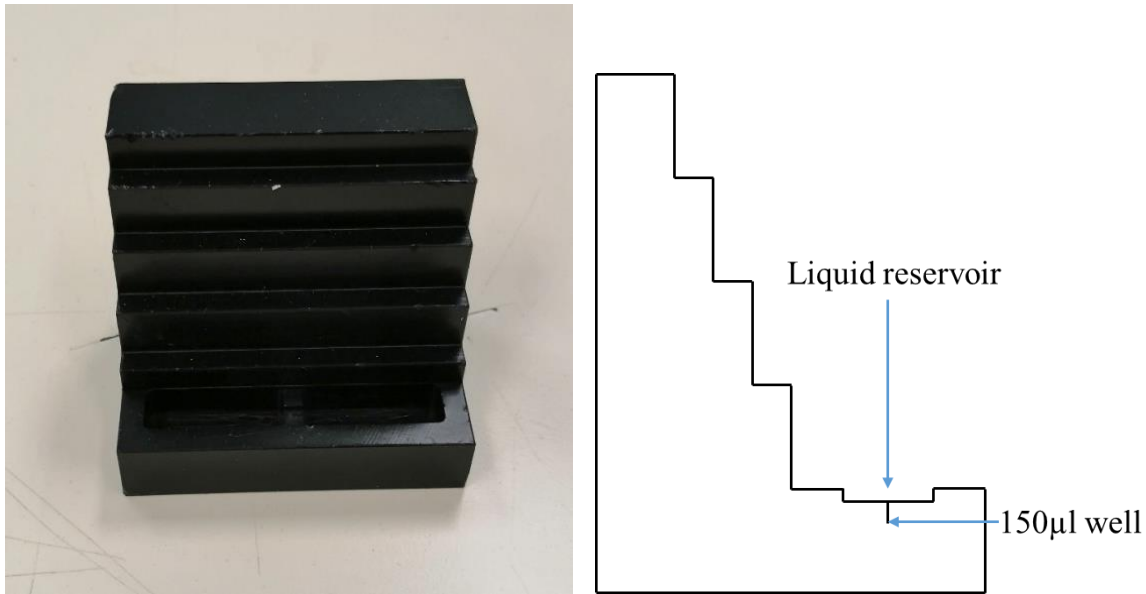


Figure 3.2: Photograph of the mantle used to hold samples during CFT measurement and a schematic illustrating the microfluidic well.

To determine the statistical significance of differences in CFT results between membrane samples, pairwise t tests were conducted and the associated P values were calculated. The t value for pairwise comparisons was calculated using Equation 1:

$$\frac{\bar{X}_1 - \bar{X}_2}{\sqrt{\left(\frac{(N_1 - 1)S_1^2 + (N_2 - 1)S_2^2}{N_1 + N_2 - 2} \right) \left(\frac{1}{N_1} + \frac{1}{N_2} \right)}} \quad \text{Equation 1}$$

where;

$\bar{X}$ is the mean for the data set;

N is the degrees of freedom for the set; and

S is the pooled standard deviation for the set.

The t tests were calculated as two-tailed hypotheses with a significance level of 0.5.

For larger groups of data, analysis of variance (ANOVA) was conducted to determine the statistical significance of differences within the group. ANOVA was calculated using Equation 2:

$$F = \frac{\sum n_j (\bar{X}_j - \bar{X})^2 / (k-1)}{\sum \sum (\bar{X}_j - \bar{X})^2 / (N-1)} \quad \text{Equation 2}$$

where;

n_j is the sample size in the j^{th} group;

$\bar{X}_j$ is the sample mean in the j^{th} group;

k is the number of groups; and

N is the number of observations in the analysis.

3.3.5 BET analysis

BET analysis was performed using a Nova 2400e surface area and pore size analyser (Quantachrome). Membrane samples were fragmented and packed into an analysis cell using a “fill rod” to reduce cell volume. A mass of 0.2 - 0.3 g was used for analysis. Prior to analysis, samples were degassed in an oven at 145 °C for 1 h. Samples were run in triplicate and the average surface area is reported. The standard deviation was calculated as a measure of the experimental error and is shown as error bars in graphs.

3.3.6 Mercury porosimetry

Mercury porosimetry was performed using an Autoscan-33 porosimeter (Quantachrome). The pore diameter D was calculated according to the Washburn equation:

$$D = \frac{-4\gamma \cos\theta}{P} \quad \text{Equation 3}$$

where θ is the contact angle between the solid and mercury, γ is the surface tension of mercury (485 dyne cm⁻¹), and P is the hydraulic pressure applied to force penetration of the mercury into the pores. A contact angle of 150° was used for the PMMA-based samples in accordance with Huinink [8].

Samples were run in triplicate and the average values for mercury intruded and dV/dP were calculated and graphed for the porogram and pore size distribution trends. The standard deviation was calculated as a measure of the experimental error and reported as error estimate in graphs.

3.3.7 ImageJ SEM analysis

SEM images were imported to ImageJ and processed to determine skin coverage on the skin layer and to estimate pore sizes on the belt layer of membrane samples.

Images are first imported to ImageJ, including a scale bar, and the scale per pixel is set by measuring the scale bar. This is achieved using the following set of commands.

1. Click the *Draw Straight Line* icon in the ImageJ tray: draw a straight line over the existing scale bar in the imported image.
2. *Analyze > Set Scale*: set the known distance to 20 and the scale to *Microns*, ensure *Global* is ticked, and click *OK*.

Following global assignment of the scale, plain images of the skin layer are imported to ImageJ and taken through the following set of commands to determine the skin coverage.

1. *Process>Sharpen*.
2. *Image>Adjust>Threshold*: the threshold is altered in the dialogue box; the second coordinate is set to 225 and the first is altered until the skinned layer is infilled, then click *Apply*.
3. *Image>Type>32 bit*.

4. *Process>Binary>Make Binary.*
5. *Analyze>Analyze Particles:* set *Size (Microns²)* to 0-1, set *Circularity* to 0-1, set *Show to Nothing*, tick *Display results*, and click *OK*.
6. The data are then exported to Microsoft Excel.
7. The total area is determined from the X and Y coordinates calculated by ImageJ and displayed in the processed image.
8. The skinned area is determined by dividing the sum of the area from step 6 by the total area calculated in step 7 and converting this to percentage coverage.

For pore analysis, plain images of the belt layer are imported to ImageJ and taken through the following steps to determine porous areas.

1. *Process>Sharpen.*
2. *Image>Adjust>Threshold:* the threshold is altered in the dialogue box; the first coordinate is set to 225 and the second is altered until the open areas are infilled, then click *Apply*.
3. *Image>Type>32 bit.*
4. *Process>Binary>Make Binary.*
5. *Analyze>Analyze Particles:* set *Size (Microns²)* to 0-1, set *Circularity* to 0-1, set *Show to Nothing*, tick *Display results*, and click *OK*.
6. The data are then exported to Microsoft Excel.
7. The data are treated and grouped in Origin and histograms are produced, bin size is set to 0.05 and plotted from 0 to 1.

The steps involved in the above operation are shown in Figures 3.3 and 3.4.

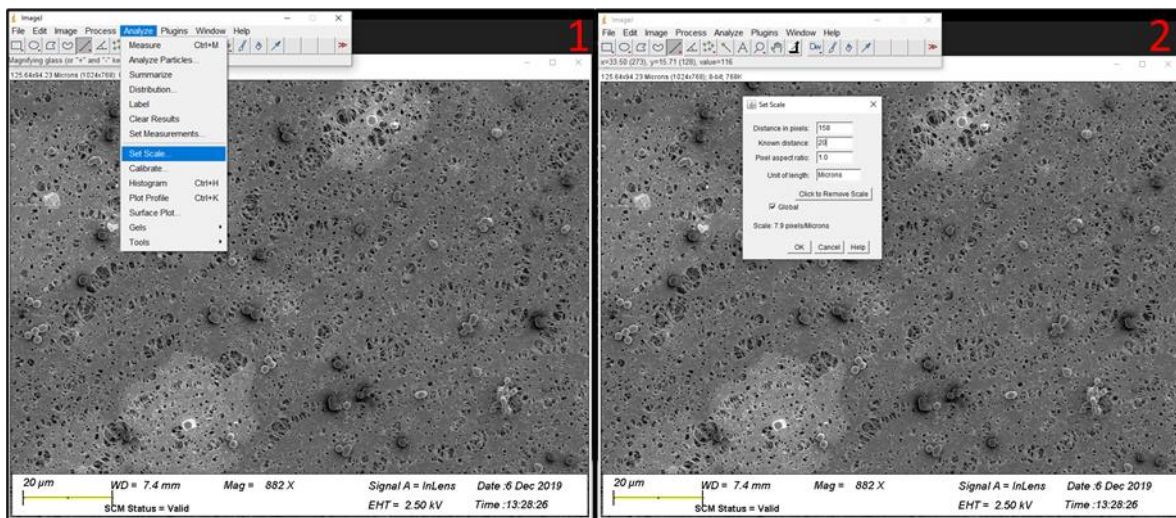


Figure 3.3: Stepwise commands involved in setting a global scale for image analysis using ImageJ.

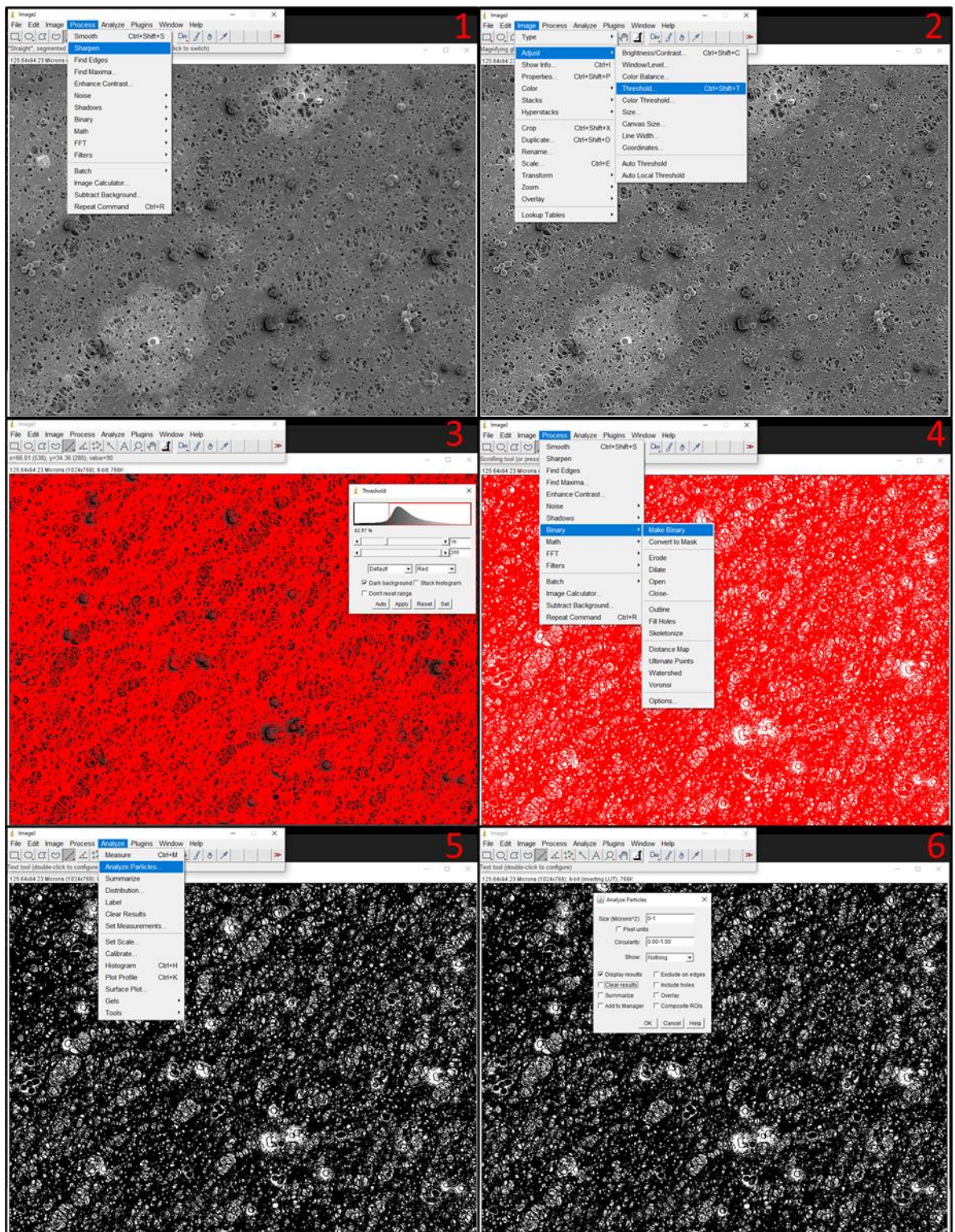


Figure 3.4: Stepwise commands involved in calculating skin layer coverage using ImageJ.

3.4 Results and discussion

3.4.1 Molecular weight analysis of PMMA

Properties of PMMA BS572 as reported by the supplier are listed in **Table 3.4**. Properties measured in house via GPC are presented in **Table 3.5**.

Table 3.4: Properties of PMMA BS572 reported by Altuglas.

Parameter	Result
T_g	118 °C
Size	300 μm
Intrinsic viscosity	170 $\text{cm}^3 \text{g}^{-1}$
Acid index	<1 mg KOH g^{-1}
Bulk density	0.7 g cm^{-3}

Table 3.5: In-house GPC results for PMMA BS572 (mean $\pm$ standard deviation).

Parameter	Result
Mn	440,549 $\pm$ 19,685.68
Mw	457,005.3 $\pm$ 23,153.5
Mw/Mn	1.037 $\pm$ 0.021

Measurement of the molecular weight of PMMA allows comparison of the results with other studies. According to the literature, PMMA membranes have previously been fabricated via an air casting method, but the PMMA used had a molecular weight of 46,400 g mol^{-1} [4]. Tsai and Torkelson used a small cell for induction of phase separation, while sulfonate was used as the only solvent and the polymer loadings were 5, 10, and 17.5 w/w% [4]. It was expected that use of a longer polymer coupled with a non-solvent–solvent system would

allow lower PMMA loading and result in more rapid demixing from the lacquer, because both polymer chain length and non-solvent concentration play a role in solubility [9]. Other studies have investigated air casting of PMMA membranes, but the casting solutions contained a second polymer such as PVDF [10] or poly(ethylene oxide) [11]. Therefore, there is not only application driven needs to develop PMMA membranes but also a significant gap in the knowledge of morphologies attainable for PMMA-only membranes.

3.4.2 PMMA drying

Data on the drying of PMMA samples over 120 h are presented in **Figure 3.5** (1-g samples) and **Figure 3.6** (10-g samples). plots of the mass loss with respect to time.

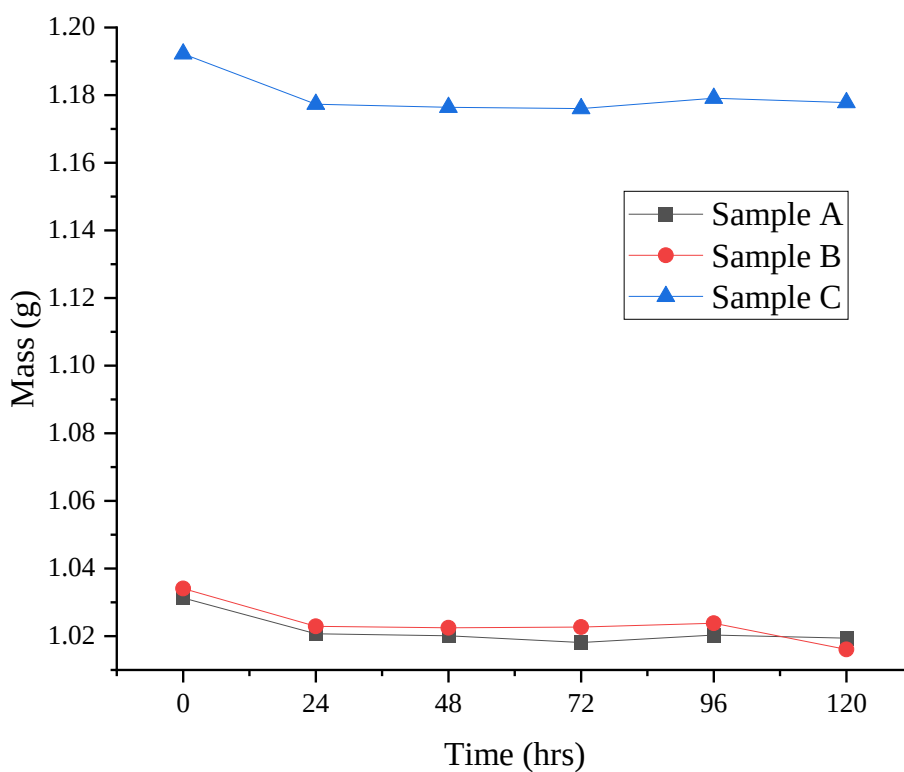


Figure 3.5: Plot of weight loss for 1-g samples of PMMA over time.

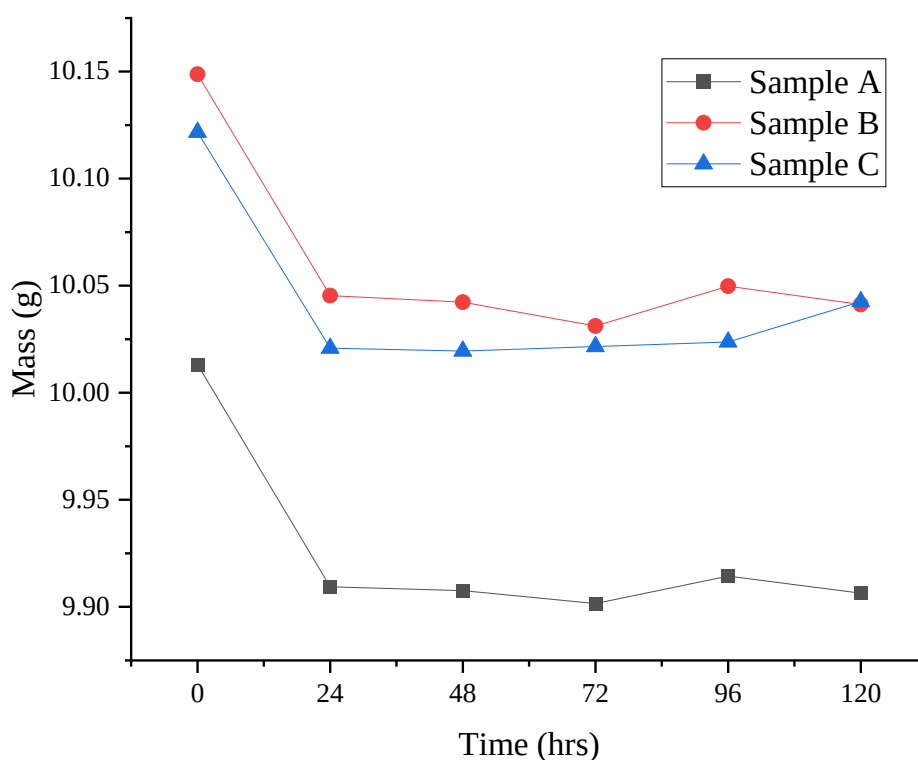


Figure 3.6: Plot of weight loss for 10 g samples of PMMA over time.

Sample masses of 1 g and 10 g were chosen to determine the water adsorbed by PMMA, which is a hygroscopic polymer. By monitoring the change in mass over time during drying it is possible to determine the percentage water in the bulk material. The source of this water is ambient air: water from humid air can be picked up throughout the supply chain from production to storage and shipping and during any other steps before use in the laboratory. For an optimised process, this water needs to be removed as it can interfere with the PMMA solubility and affect the final membrane products. As will be seen below, membrane formation is highly dependent on the presence of water. A drying temperature of 60 °C was chosen as this is well below the T_g value of 118 °C (**Table 3.4**) reported by the supplier, so drying at this temperature should prevent transition to a viscous and rubber-like state that could affect the PMMA behaviour in the lacquer formulations [5].

The data in **Tables 3.4** and **3.5** show that no significant mass loss was observed after 24 h; any slight variations in mass thereafter can be attributed to the precision and tolerance of the analytical balance. From the data gathered, the percentage water on the surface of PMMA appears to be between 0.78% and 1.741%; besides the margin of error, this 1% difference may be attributable to the rate of adsorption of water molecules. The rate of adsorption will be proportional to the vapour pressure and the square of the number of vacant sites [5]. In the case of PMMA, vacant sites are assumed to be on the ester group of the side chain [12]. As the polymer is purchased as microbeads, the number of active sites will be severely limited by the available surface area (since PMMA is hydrophobic, swelling is very limited), so only a fraction of the sites will be available for adsorption. Ambient humidity is a source of water molecules for potential adsorption. For water adsorption onto PMMA, a potential active site needs to be in the right orientation, the relative humidity needs to be favourable, and the water vapour pressure needs to be sufficient to allow a collision to result in adsorption of a water molecule [5]. Variations in these factors could explain the ~1% difference in results for the water content.

3.4.2 Lacquer characterisation

Ethanol and butanol were chosen for the solvent system because of the swelling behaviour exhibited by PMMA in low-molecular-weight alcohol solutions, as reported by Papanu et al. [13]. Acetone is a solvent widely used for PMMA [14,15]. The combination of ethanol, butanol, and acetone allows the formation of a highly swollen gel when the lacquer phase separates, resulting in a highly porous membrane structure. Lacquers were characterised to determine the effect of PMMA loading on the turbidity of the lacquer solution with respect to temperature. By mapping changes in turbidity via measurement of light scattering, the cloud point of a solution can be determined as the point of inflection of a plot of turbidity

versus temperature. This is not strictly the classic definition of the cloud point, which is the temperature or non-solvent concentration at which a 1% w/w polymer solution becomes turbid due to the onset of phase separation [16,17]. For samples cast with a polymer concentration higher than 1% w/w for a TIPS system, the drastic increase in turbidity can be deemed the cloud point as it coincides with the nucleation point for the formation of solid-phase polymer. This is the point at which the polymer chains no longer have sufficient energy to detangle, so the solution ceases to be a single homogeneous phase and becomes two distinct phases, giving rise to the cloudiness observed in vial B in **Figure 3.7**. This phenomenon can be explained by critical solution theory in terms of the upper critical solution temperature (UCST) [18]. As the lacquer samples contain a large proportion of non-solvent (ethanol and butanol), demixing is observed when the UCST is reached. This results in separation of the components into two different phases. As PMMA and the two non-solvents are chemically dissimilar, this separation can be attributed to low entropies of mixing, which occurs because the bonds between monomer subunits hinder the polymer chains from spreading throughout the entire system [18]. The effect can be attributed to both the molecular weight and the temperature of the solution; as the PDI of the PMMA used is close to 1, it can be assumed that temperature is the only variable that will influence solubility. It is evident from the results in **Figure 3.8** and **Figure 3.9** that the solubility decreased as the PMMA concentration increased.

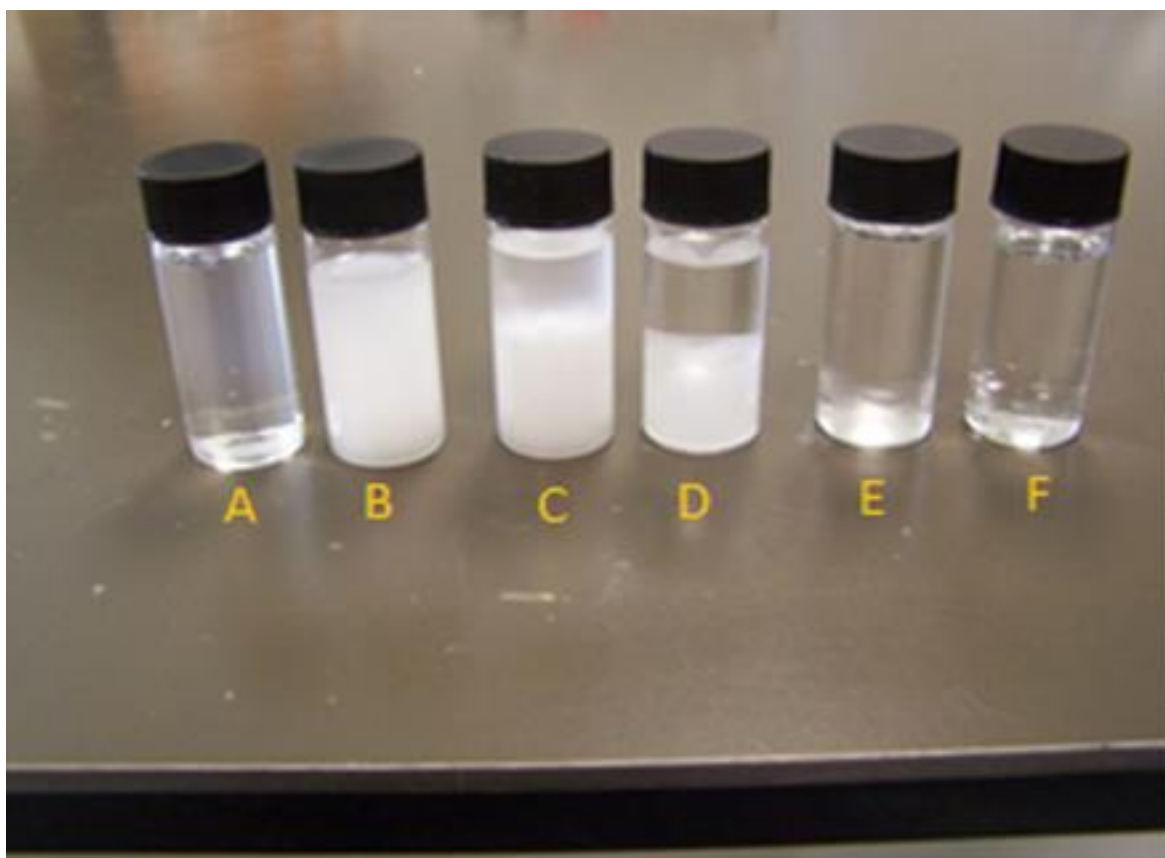


Figure 3.7: Lacquer transition stages during cooling. A, homogeneous lacquer above the cloud point; B, turbid lacquer as the cloud point is reached; C, contraction of the polymer as the temperature decreases below the cloud point; D, further contraction of the polymer and the beginning of gelation; E, gelation and major contraction; and F, fully contracted and gelated PMMA.

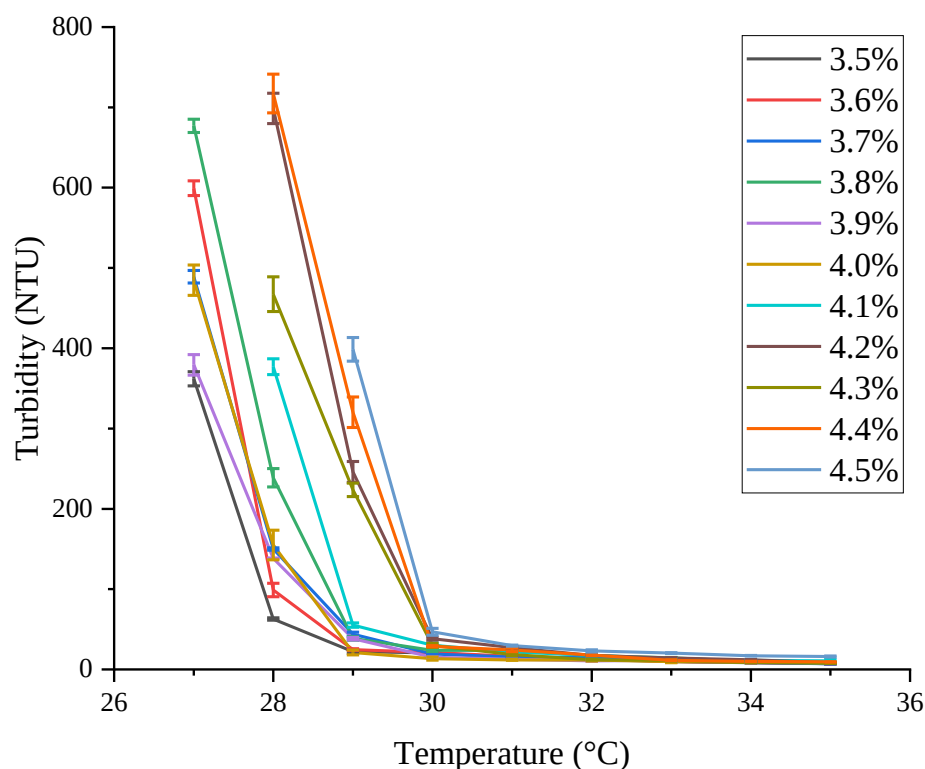


Figure 3.8: Turbidity versus temperature for lacquers formulated with 3.5–4.5% w/w PMMA.

Figure 3.8 shows the change in turbidity with respect to temperature for the first series of lacquers prepared. In this case loading was on a percentage PMMA basis and for every 0.1% increase in PMMA the acetone was decreased by 0.1%. The ethanol and butanol concentrations were kept constant, as these non-solvents drive the phase separation. As already noted, the combination of acetone, butanol, and ethanol provides a UCST system for PMMA, and thus it was expected that the cloud point would increase with the PMMA concentration [18]. It is evident from **Figure 3.8** that the point of inflection for turbidity versus temperature (taken as the cloud point, as explained earlier) varies with the PMMA concentration. For the second series of samples with lacquers formulated on a mass basis with higher PMMA concentrations (2.5, 5, 7.5, and 10 g of PMMA per 100 mL of solvent

mix), the increase in inflection point/cloud point with the PMMA concentration is even more pronounced, as observed in **Figure 3.9**.

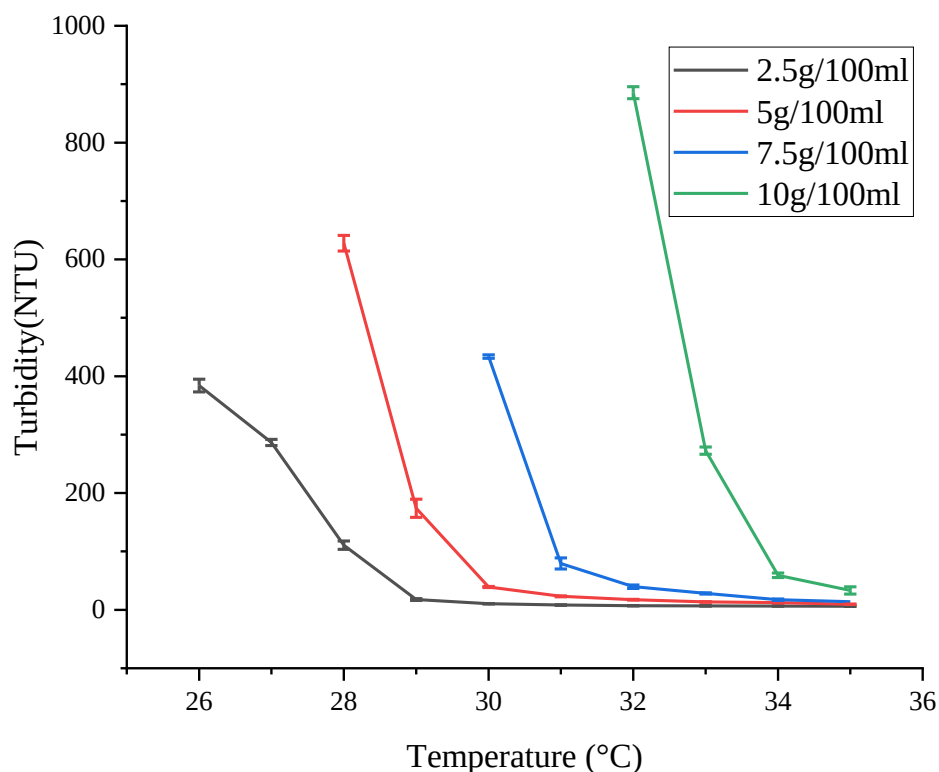


Figure 3.9: Turbidity versus temperature for samples cast with PMMA loading of 2.5–10 g per 100 mL of solvent.

The curves in **Figure 3.9** show that, on average, the cloud point increases by 2 °C for each 2.5 g incremental addition of PMMA to 100 mL of solvent mix. This is as expected because the solubility of the polymer is the limiting factor. The data show that there is a linear correlation between the cloud point and the PMMA concentration until the solubility limit is reached. A sample containing 12.5 g of PMMA per 100 mL of solvent mix was also prepared, but its properties were consistent with those of a gel rather than a true lacquer, as the solution was notably viscous. Therefore, characterisation was difficult because of rapid

phase separation when the temperature reached 36 °C. This might correspond to the gel boundary in the phase diagram for this PMMA; similar boundaries have been reported previously, with the most prominent system being acetone–cellulose acetate [16,17]. This suggests that for this temperature range there is an upper limit for the PMMA concentration in lacquers that are viable as casting solutions.

The turbidity results can be explained in terms of polymer–solvent and polymer–polymer interactions. When the lacquer is held at a temperature above the cloud point, there is sufficient energy to allow detanglement of polymer chains, leading to a dispersed, clear solution in which polymer–solvent interactions are the dominant intermolecular forces. However, when the temperature drops below the cloud point, polymer–polymer interactions take over and become the dominant intermolecular forces in the solution and thus nucleation occurs. This is because PMMA is freely soluble in acetone but is partly soluble or insoluble in both ethanol and butanol (concentration and temperature dependent); mixing of the three yields a compound solution that acts as a solvent for PMMA. This can be explained in terms of the Hansen solubility parameters described in Chapter 1, whereby each component of the solution contributes to the dispersion, polar, and hydrogen bonding forces that determine a whether a polymer is soluble in a given solvent mix [19,20]. In the case of the mixture of solvent and non-solvent, the resulting solution will be more likely to undergo liquid–liquid demixing as a result of temperature decrease, that is, for TIPS to occur [21,22]. The transition from soluble (clear) to insoluble (turbid) can be seen in **Figure 3.7**. When allowed to cool below the cloud point, a lacquer goes through a number of stages that can be broadly described as nucleation, contraction, and gelation. This corresponds to decreasing Gibbs free energy as polymer–polymer interactions dominate and lead to entanglement of PMMA chains, eventually resulting in precipitation of the PMMA as a highly swollen gel (**Figure 3.7F**). This can be quantified by applying Flory–Huggins solution theory and the entropy of the system can be further probed [23].

Following cloud point analysis, samples composed of 3.7% and 4.2% PMMA were chosen for optimisation of the air casting process. It was hypothesised that the variation in cloud point between these two samples coupled with the slight increase in PMMA loading should lead to a difference in pore morphology. Following process optimisation, it was observed that the 4.2% sample had a faster capillary flow time, so further samples were prepared using the same solvent mix ratio and loaded with PMMA masses ranging from 2.5 g to 10 g. In this way the solvent mixture was kept constant, and the only variable was the PMMA weight loading. This allowed confirmation of the effect of PMMA loading on pore morphology.

3.4.3 Membrane appearance

Membranes cast from lacquers containing 3.7% and 4.2% PMMA and 2.5 and 5 g of PMMA per 100 mL of solvent were matte white in appearance, with occasional cracking and delamination observed at the edges. When removed from the Melinex backing, these membranes were flexible but quite relatively fragile and brittle, with tearing occurred when even low force was applied. By contrast, the membranes cast from lacquers containing 7.5 and 10 g of PMMA per 100 mL of solvent were glossy and white, and the 10g samples had an almost translucent appearance for the surface layer. These membranes exhibited a greater degree of delamination, originating at the edges and extending towards the centre. When removed from the backing, the membranes were inflexible and quite rigid, and when excess force was applied, they showed brittle fracture typical of a glassy polymer.

The delamination seen in samples is most likely caused by changes in surface tension as the lacquer phase separates. As the lacquer phase separates and sets as a membrane, the PMMA transitions from a swollen gel state to an unswollen state [13]. This phase change is likely to be the reason for the delamination observed at the edges, and it has been reported that surface tension effects play a role in macrovoid formation [24,25].

PMMA is an amorphous polymer and thus the polymer units will be arranged as a randomly packed structure [26]. The opaque appearance of the membranes cast from 3.7% and 4.2% PMMA and 2.5 and 5 g of PMMA per 100 mL of solvent mix can be attributed to random packing of chains at the surface [26] combined with the bulk porosity. By contrast, the glossy appearance of the 7.5 and 10 g membranes is probably due to closer packing of PMMA, leading to a transparent layer at the air interface, as observed in SEM images and described in Section 3.4.4.

The tearing and breaking observed can probably be attributed to the glass transition temperature (T_g) of PMMA, which is 118 °C [27]. T_g is the temperature below which carbon chains are rigid. In this state, the polymer chains can be thought of as frozen in place [28] and, therefore, it would be expected that any membranes fabricated from PMMA alone would be brittle.

3.4.4 SEM Imaging

SEM (**Figure 3.10** and **Figure 3.11**) revealed that the membranes had a macroporous structure with significantly less porous skin layers. The SEM images in the three planes indicate that the membranes can be characterised as asymmetric [29,30]. Asymmetric membrane structures have been produced in other studies. However, Cheng et al. produced asymmetric PMMA membranes using a wet phase-inversion method [1], while Tsai and Torkelson produced asymmetric PMMA membranes using a thermally driven process [4]. In addition, as previously noted, these studies used PMMA of much lower molecular weight, which may affect the resulting membrane morphology.

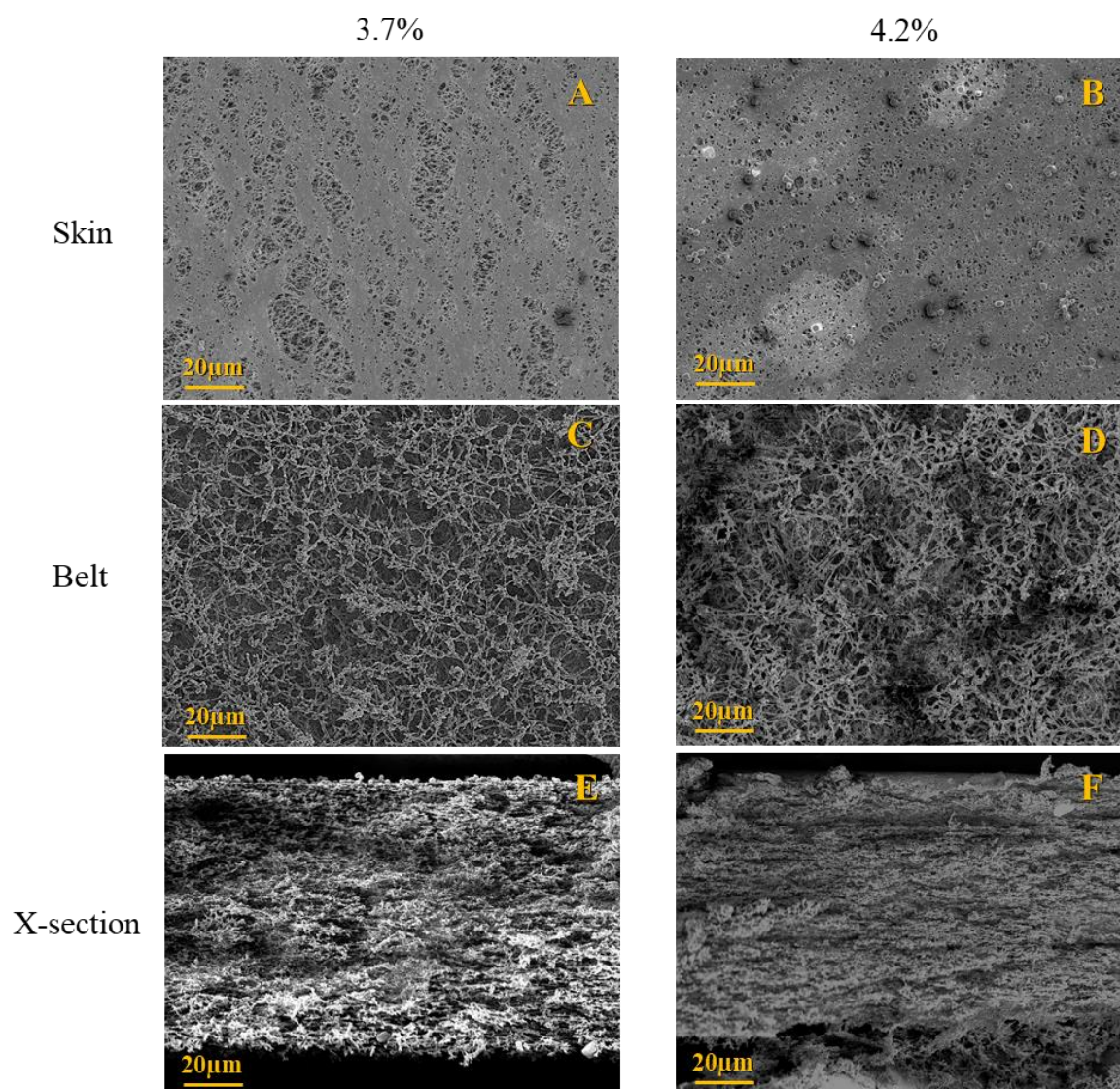


Figure 3.10: SEM images of the skin and belt surfaces and cross-sections of membranes cast from lacquers containing 3.7% and 4.2% PMMA.

Visually, the pilot membranes cast with 3.7% and 4.2% PMMA look quite similar; both have a skin layer that is noticeably less porous than the bulk, but with a greater pore density underlying the layer that is visible through the defects present. The only discernible difference is the appearance of some spherical particulates on the surface of the 4.2% sample, which may be an artefact following washing of the membrane in water to remove residual solvents. Skinning to some degree should be expected, as the polymer will migrate towards the air interface during phase separation [31], resulting in a more polymer-rich region at the air–lacquer interface. As phase separation continues, a more densely packed structure is

formed. This phenomenon is often seen in asymmetric membranes and is specifically classified as a Loeb–Sourirajan or integrally skinned asymmetric membrane/structure [32,33].

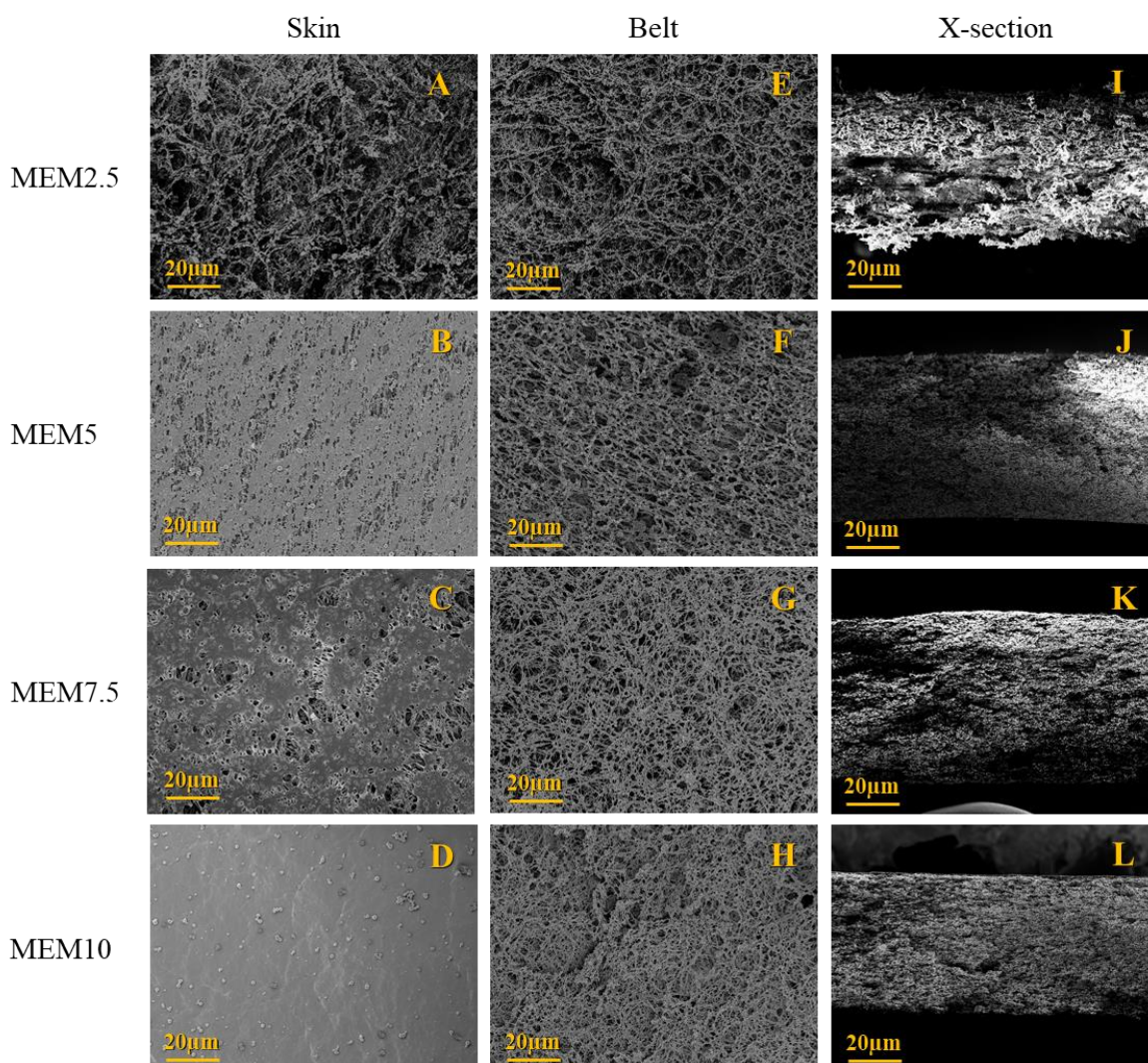


Figure 3.11: SEM images of skin and belt surfaces and cross-sections of PMMA membranes cast from lacquers containing 2.5–10 g of PMMA per 100 mL of solvent mix.

With the exception of sample MEM2.5 (**Figure 3.11A**), all the samples cast from lacquers formulated with PMMA on a percentage basis had a very thin skin layer. In the case of samples MEM5 and MEM7.5, a more porous structure was visible through defects in the

skin layer (**Figure 3.11B,C**), while sample MEM10 showed complete skinning, with some of the PMMA crystallised as spheres on the skin surface (**Figure 3.11D**). This change in surface morphology with increasing PMMA concentration is as expected. Skin layer formation is associated with high local concentrations of polymer during the phase separation process. As the polymer phase separates, it will precipitate out of solution as a highly swollen gel due to the presence of non-solvents [21]. Following precipitation and commencement of evaporation, the solvents and non-solvents trapped in the gel phase will migrate from the substrate side to the air side, and in doing so carry polymer with it. This results in a localised region with a high polymer concentration. As evaporation continues, this region densifies and becomes nonporous, leading to skin layer formation [31]. In the case of samples cast with a higher concentration of PMMA, more of the bulk polymer is carried towards the surface, leading to progressively more skinning with respect to polymer concentration. The lack of any skinning for sample MEM2.5 may be indicative of a critical point between 2.5 and 5 g of PMMA at which skinning will occur [31]. This hypothesis is also supported by the appearance of the skin layers in membranes cast from samples containing 3.7% and 4.2% PMMA. In the case of MEM2.5, the lower concentration of PMMA led to a lower cloud point, as shown in **Figure 3.9**. This lower cloud point combined with casting conditions will in theory lead to slower phase separation [34], which in turn may influence the solvent outflow, reducing it to a rate that prevents skin layer formation [31]. In general, high solvent outflow is associated with increasing local polymer concentrations at the air interface [31]. Thus, in the case of sample MEM2.5, lower solvent outflow prevented mass migration of polymer from the substrate side to the air side, so a polymer-rich region did not form at the air interface.

The belt layer was much more porous and open than the skin layer (**Figure 3.11E–H**). Bulk migration of the polymer towards the air interface during phase separation leaves a solvent-rich and polymer-lean region close to the belt, leading to higher porosity and quite an open

morphology [23,29]. This is the opposite effect to that observed for the skin layers. Following precipitation, the substrate interface is the one most likely to experience high solvent outflow, as it is in direct thermal contact with the heated bed. This results in polymer migration through the gel phase and the formation of a polymer-rich region at the air interface [31].

Cross-sectional images reveal an overall porous morphology with a disordered appearance (**Figure 3.11I–L**). In addition, skinning is visible for the samples containing 5–10 g of PMMA per 100 mL of solvent mix (**Figure 3.11J–L**). While it is difficult to give a precise estimate of the overall bulk porosity, it is evident that, excluding the skin layer, the membranes all contain bulk porosity of varying degrees; such morphology should be expected for integrally skinned asymmetric membranes [29,31].

Images for the two sets of samples reveal similar structures: all have a more porous belt layer and, excluding sample 2.5g, all have some degree of a skin layer. Furthermore, all appear to have an asymmetric morphology when looking at the bulk membrane in cross-section. The point at which skinning occurs may lie between 2.5 g of PMMA/100 mL and 3.7% PMMA (equivalent to 3.84 g/100 mL). Further experiments could be carried out to determine the exact point at which skinning starts.

3.4.5 Mercury porosimetry

Porograms and pore size distribution graphs for the 3.7% and 4.2% PMMA samples and the samples with increasing PMMA mass (2.5–10 g PMMA/100 mL of solvent mix) are shown in **Figures 3.12–3.15**.

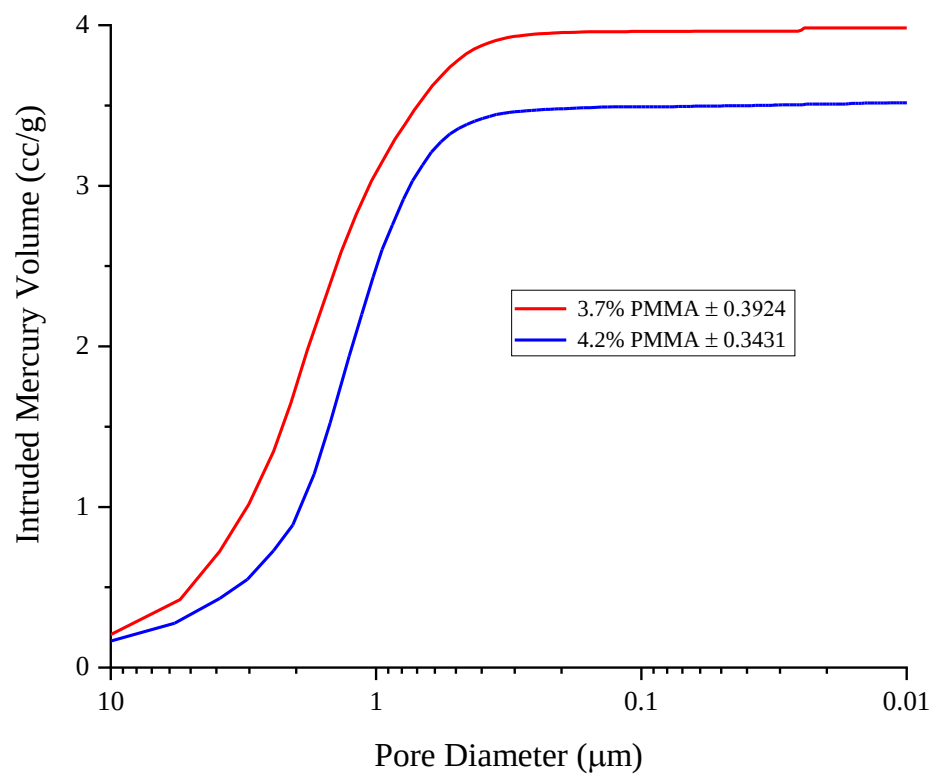


Figure 3.12: Porograms for membranes cast from samples containing 3.7% and 4.2% PMMA.

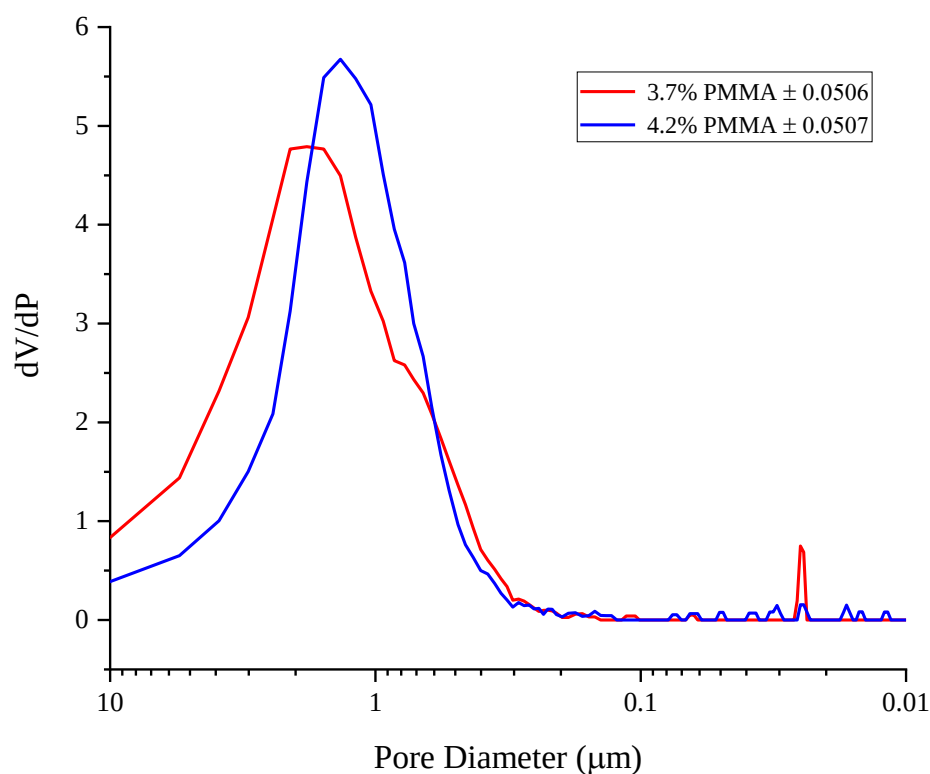


Figure 3.13: Pore size distribution for membranes cast from samples containing 3.7% and 4.2% PMMA.

Figure 3.12 shows that there was a slight decrease in pore volume when the percentage PMMA was increased from 3.7% to 4.2%. This is most likely because of the difference in pore size distribution observed in **Figure 3.13**. The average pore size observed was 1.81 and 1.35 μm for the 3.7% and 4.2% samples, respectively.

The pore range is broader for the 3.7% sample and there are a number of pores in the 2–10 μm range, as well as a prominent peak in the nanometer range. By contrast, the 4.2% sample has a narrower pore distribution overall and while it contains some nanopores, they are not as concentrated as the peak detected for the 3.7% sample. This is most likely because of the packing of PMMA as the phases separate in the samples: it would be expected that the 3.7% sample would have a more open porous structure, as the lower PMMA concentration would lead to less polymer packing, in particular near the skin side of the membrane.

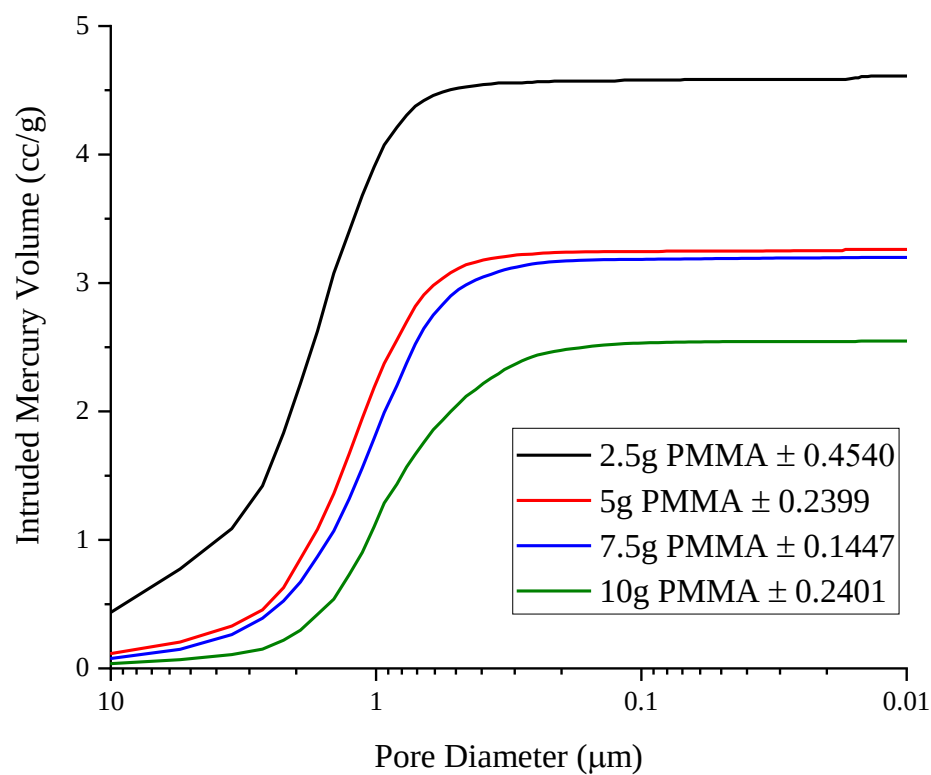


Figure 3.14: Porograms for the membranes cast from samples containing 2.5–10 g of PMMA per 100 mL of solvent mix.

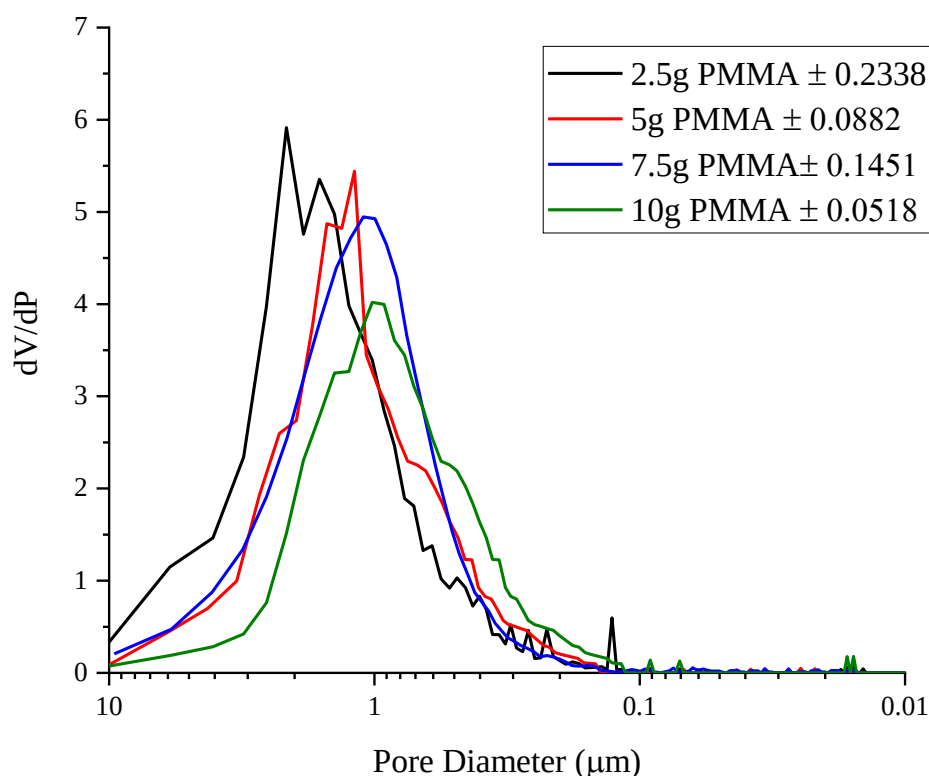


Figure 3.15: Pore size distribution for the membranes cast from samples containing 2.5–10 g of PMMA per 100 mL of solvent mix.

For the sample series containing 2.5–10 g of PMMA per 100 mL of solvent mix, in general the pore volume decreases as the PMMA concentration increases. The most drastic change is evident for doubling of the PMMA concentration from 2.5 g to 5 g per 100 mL, while minor changes in pore volume are evident as the PMMA concentration increases from 5 to 7.5 to 10 g. These changes can be attributed to tighter packing of PMMA as phase separation occurs [1,4]. It is evident from **Figure 3.15** that the pore diameter range for samples 5g, 7.5g, and 10g has a broad peak around 1 μm that stretches into the nanometre region, while for sample 2.5g there are only a few pores in the nanometre region and a sharp peak at $\sim 2 \mu\text{m}$, which probably gives rise to the higher pore volume. The average pore size observed was 1.61, 1.18, 1.01, and 0.91 μm for the 2.5g, 5g, 7.5g, and 10g samples, respectively.

Similar changes in pore size have been observed in the case of high-density polyethylene and polyetherimide: Bakeri et al. noted that an increase in polymer loading led to a decrease in pore size [35], while Akbari and Yegani reported that as the polymer concentration increased, the mean pore diameter decreased [36], in agreement with the trends observed in **Figure 3.15**.

3.4.6 BET data

Surface area results for the membranes produced from the two different sample series are presented in **Table 3.6** and **Table 3.7**.

Table 3.6: Surface area results according to BET measurements for the 3.7% and 4.2% PMMA membranes.

Sample	Surface area ($\text{m}^2 \text{g}^{-1}$)
3.7% PMMA	7.6 ± 0.16
4.2% PMMA	6.8 ± 0.29

Table 3.7: Surface area according to BET measurements for the membranes cast from samples containing 2.5–10 g of PMMA per 100 mL of solvent mix.

PMMA sample	Surface area ($\text{m}^2 \text{g}^{-1}$)
MEM2.5	2.2 ± 0.05
MEM5	5.7 ± 0.12
MEM7.5	7.8 ± 0.29
MEM10	9.4 ± 0.25

As observed from **Figure 3.13**, the 3.7% sample had a broader pore size distribution compared to the 4.2% sample, which is most likely the reason for its higher surface area. In addition, the 3.7% sample exhibited a distinct peak in the nano region of the pore size

distribution in **Figure 3.13**, which would be expected to be reflected in an increase in the surface area. While some nanostructures were also evident for the 4.2% sample, they were not present in the same quantity as observed for the 3.7% sample.

Samples MEM2.5–MEM10 show a general trend of increasing surface area as the PMMA concentration was increased. This general trend is partly as expected: as the PMMA concentration is increased, the packing would be expected to be tighter, leading to a smaller average pore size. Consequently, membranes cast with a higher concentration of polymer will be less porous than those cast with lower polymer concentrations [37]. This decrease in pore size has already been demonstrated with the pore size distribution (**Figure 3.15**).

The one exception in this case is sample MEM7.5, which exhibited a decrease in surface area relative to MEM5. The pore size distribution in **Figure 3.15** provides evidence to explain this result. In contrast to samples MEM5 and MEM10, sample MEM7.5 has a larger concentration of pores of $>2\ \mu\text{m}$ and a lower concentration of pores of $<1\ \mu\text{m}$. This results in a lower surface area in comparison to MEM5. This may be due to the sensitive nature of the membrane formation process. Solvent evaporation, or specifically non-solvent evaporation, affects pore formation. In the case of MEM7.5, there may have been a temperature variation that was not detected during membrane formation that led to an increase in non-solvent evaporation while the sample was curing [30]. This increase would explain the increase in pores $>2\ \mu\text{m}$ in comparison to samples MEM5 and MEM10.

3.4.7 ImageJ SEM analysis

Results for skin coverage for the samples are presented in **Table 3.8**. The SEM images presented in **Figures 3.10** and **3.11** were used for analysis. As described in **Section 3.3.7**, the images were sharpened prior to analysis to allow easier detection of skin boundaries and defects in the skin layer when processing the images and give greater accuracy in measuring the skin coverage.

Table 3.8: Percentage skin coverage for PMMA membrane samples cast at 3.7%, 4.2%, and 2.5–10g.

Sample	Skin layer coverage (%)
3.7%	64.60
4.2%	84.71
Mem 2.5	4.40
Mem 5	77.75
Mem 7.5	84.08
Mem 10	100*

*3.17% of the surface comprises PMMA particulates; the surface remains completely skinned.

The results in **Table 3.8** show a general trend of an increase in skinning with increasing PMMA concentration, as evident from the SEM images shown in **Figures 3.10** and **3.11**. Use of ImageJ allowed quantification of the increase in skinning with increasing PMMA concentration. As mentioned previously, the increase in skin layer coverage is as expected, as an increase in PMMA concentration leads to tighter packing at the air–lacquer interface, resulting in a more pristine skin layer [31]. A noteworthy finding is the formation of PMMA particles on the surface of the 10g sample (**Figure 3.11D**). Quantification revealed that these PMMA particles accounted for 3.17% of the surface coverage. Interestingly, the 3.7%

sample appears to fall in line with the general trend of increasing skinning as the polymer concentration increases, while the 4.2% sample exhibited greater skinning in comparison to the 5g sample (equivalent to 4.76% PMMA loading), which may be attributable to the somewhat random distribution of pores when using solvent evaporation as the pore formation mechanism.

Figures 3.16 and **3.17** show histograms of the pore sizes detected using ImageJ for the 3.7% and 4.2% PMMA membranes, and the 2.5–10g PMMA membranes, respectively.

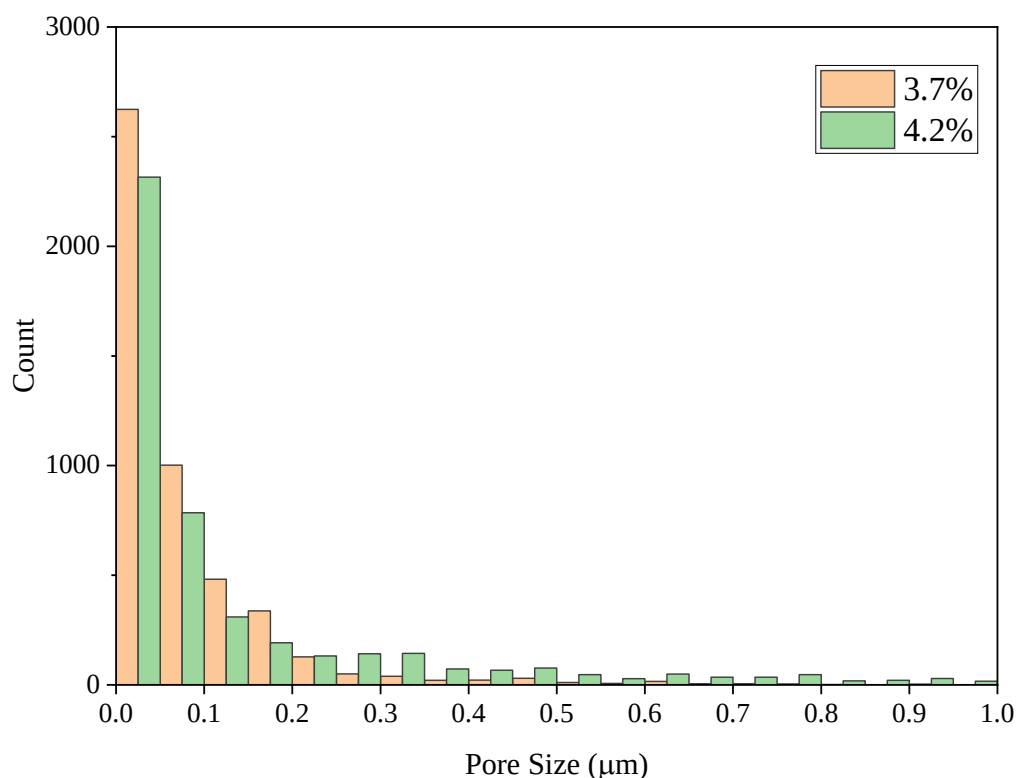


Figure 3.16: Histogram of pore sizes detected using ImageJ for membranes cast at 3.7% and 4.2% PMMA.

The results in **Figure 3.16** show higher nanopore counts for the 3.7% sample up to 200 nm in comparison to the 4.2% sample, with higher counts for pores >200 nm for the 4.2% sample. This is in agreement with the mercury porosimetry data and the PSD results presented in **Figure 3.13**. There was a higher and narrower peak at 20–30 nm for the 3.7%

sample, whereas the 4.2% sample showed multiple nanostructures from 1 μm to 10 nm region (**Figure 3.13**), in accordance with the greater number of pores from 200 nm to 1 μm for the 4.2% sample in **Figure 3.16**.

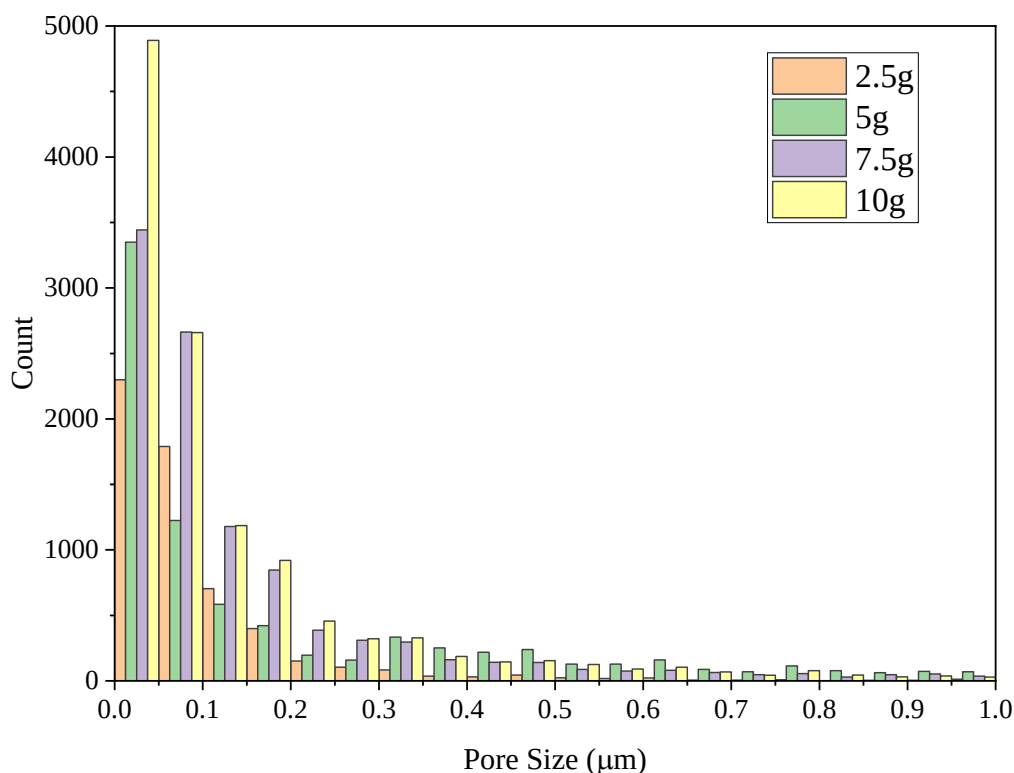


Figure 3.17: Histogram of pore sizes detected using ImageJ for 2.5–10g PMMA membranes.

The data presented in **Figure 3.17** show increasing nanopore formation as the PMMA concentration is increased, in agreement with the PSD data shown in **Figure 3.15**. As previously discussed, this arises due to closer packing of PMMA molecules as phase separation occurs. In the case of samples 5, 7.5, and 10g, more nano structures are observed which is in agreement with the PSD in **Figure 3.15**, all three samples showed some nanostructure formation with some broad and narrow peaks observed below the 50nm region.

Although SEM image analysis has been utilised by others for pore measurement [38,39], it should not be the sole method used in analysing pore sizes or distributions, and should be applied in combination with both mercury porosimetry and BET analyses, as the three techniques together provide greater insights into the differences in CFT for variations in the process parameters.

ImageJ shows good ability in measuring skin coverage for polymer membranes, and has previously been used for other analyses such as pore size, nodule size, and surface roughness [38,39]. The skin layer of a membrane typically exists within one plane, so it is relatively easy to create a binary image, as the contrast and colour of the skin layer tend to be fairly consistent, allowing a good degree of accuracy for calculation of skin layer coverage. Although ImageJ can yield a good estimate of potential pore sizes from SEM images, there are some drawbacks. The analysis relies on creation of a binary image from the SEM image, which can be difficult if the contrast varies from layer to layer for 2D rendering of a 3D structure, as is the case when looking at the belt layer of aircast PMMA membranes. Any variation in contrast can lead to difficulties when setting a threshold level to create a binary image, as each layer will be shaded differently to the layer above it, so pores visible between multiple levels may be difficult to quantify. An alternative method for looking at the red, green, blue composition could be utilised [40]; however, as SEM images are typically captured in greyscale, creation of a binary black and white image is more pragmatic. The ImageJ technique should therefore be applied in tandem with a physical quantification method such as mercury porosimetry to account for and quantify pores in both two and three dimensions.

3.4.8 Capillary flow time

CFT results for the PMMA membranes are summarised in **Table 3.8** and **Table 3.9**.

Table 3.9: CFT data obtained for the 3.7% and 4.2% PMMA membranes.

Sample	Capillary flow time (s)			
	A	B	C	Mean
3.7%	282	237	221	246.6
4.2%	197	231	223	217

As observed from **Table 3.9**, the CFT time decreased when the weight percentage of PMMA was increased from 3.7% to 4.2%. This may be explained by the mercury porosimetry data in **Figure 3.13**. The 4.2% sample has a smaller average pore size and a narrower pore size distribution, with only minor peaks in the nanometre region. By contrast, the 3.7% sample has a broader pore size distribution and a distinct peak in the nanometre region. This difference in pore size distribution is most likely the reason for the difference in CFT. It would be expected that a membrane with a narrower pore size distribution would exhibit a faster CFT as there would be less variation in pore size and thus more uniform flow through the membrane. Conversely, a membrane with a broader pore size distribution would be expected to have a slower CFT as the flow rate would be limited by the smaller range of pores in the overall bulk morphology. This will be especially true for samples with nanopores leading into micropores [14].

Table 3.10: CFT data obtained for the membranes cast from samples containing 2.5–10 g of PMMA per 100 mL of solvent mix.

Sample	Capillary flow time (s)			
	A	B	C	Mean
2.5g	217	281	222	240
5g	425	456	401	427.33
7.5g	518	513	522	517.67
10g	1200*	1200*	1200*	1200*

*Test stopped after 1200 s as movement of solvent front could not be detected.

The results in **Table 3.10** reveal that CFT increased with the PMMA loading. This increase in CFT can best be explained by the change in pore size observed in **Figure 3.15**: as the pore size decreases, CFT will increase because pore filling is restricted by smaller pores adjacent to larger pores [14]; the flow rate will always be limited by the size and relative abundance of smaller pores. In general, the results show that a narrower pore size distribution (sample 2.5g in **Figure 3.15**) will yield a faster lateral flow rate than a sample with a broader pore size distribution (samples 5g, 7.5g, and 10g in **Figure 3.15**).

In the case of sample 10g, testing was stopped after 1200 s as no further wicking was observed: wicking was observed to a height ~ 0.5 mm and then ceased. This might be because of the large proportion of nanosized pores, which may affect the balance between cohesion forces among components of the solution and the adhesion forces that drive capillary flow. Gravity also plays a role in resistance to flow, and the combination of gravity and cohesive forces in the presence of abundant nanosized pores may have prevented lateral flow above the ~ 0.5 mm observed. Another factor that may contribute to the lower flow may be the pristine skin layer observed for sample MEM10 in **Figure 3.11D**. As the skin layer is densely packed and shows no defects, the transport rate will be hindered as the area into which liquids can permeate will be significantly smaller [41]. While other samples exhibited skin layers,

the SEM images presented in **Figures 3.10** and **3.11** show that, in contrast to sample MEM10, these skin layers had defects and the more porous sublayers were also visible.

Comparison of the two sets of data in **Table 3.8** and **Table 3.9** shows that the CFT results for the optimisation samples fall in between those for the 2.5g and 5g samples, as the relative PMMA loading is between these values. The optimum PMMA concentration for the fastest CFT appears to be between 3.7% and 5 g (5 g equates to 4.76% loading) as the 4.2% sample had the fastest CFT. The optimum is likely to be closer to 4.2%, however, as the CFT drastically increased to >400 s for equivalent loading of 4.76%.

Statistical analysis results for the CFT data in relation to the PMMA concentration are shown in **Tables 3.11 and 3.12**.

Table 3.11: Results for t-test pairwise comparisons of capillary flow time in relation to the PMMA concentration

Sample comparison	T Value	P Value	Statistically Significant
3.7 v 4.2%	1.41627	0.22964	No
3.7% v 2.5g	0.2425	0.820319	No
3.7% v 5g	7.45762	0.001727	Yes
3.7% v 7.5g	14.69224	0.000125	Yes
4.2% v 2.5g	1.00126	0.373359	No
4.2% v 5g	11.10441	0.000374	Yes
4.2% v 7.5g	28.39625	<0.00001	Yes
2.5g v 5g	7.20631	0.001966	Yes
2.5g v 7.5g	13.40414	0.000179	Yes
5g v 7.5g	5.59984	0.004993	Yes

The results show that for the ten comparisons made, the difference in CFT was statistically significant for seven and was not statistically significant for three. For the pairwise comparisons that did not have a statistically significant difference in CFT, the differences in PMMA concentration were 0.5% (3.7% vs 4.2%), 1.27% (3.7% vs 2.5g), and 1.77%

(4.2% vs 2.5g). It is possible that for these samples the weight/weight percentage of PMMA alone is not the sole reason for the difference in CFT and that the difference in skinning across these three samples may also have led to the variation in CFT. In the case of the trend for 2.5g–10g, only samples of 2.5, 5 and 7.5 g of PMMA were tested, as the CFT test failed for 10g samples (incomplete wicking) across multiple specimens. All comparisons showed statistical significance for this trend, meaning that the changes in CFT can be attributed to differences in the PMMA concentration.

To supplement the pairwise t-test comparisons, ANOVA within-group testing was also carried out to determine the statistical significance of differences in CFT for the two data sets overall. The ANOVA results are presented in **Table 3.12**.

Table 3.12: ANOVA for within-group comparison of capillary flow time in relation to the PMMA concentration for two groups of membrane samples

Data set	F-statistic value	P-value	Statistically Significant
2.5g-7.5g	88.16354	0.00004	Yes
2.5g-7.5g, 3.7% 4.2%	50.82546	0	Yes

For the 2.5–7.5g group, the difference in CFT was found to be statistically significant, suggesting that the difference in PMMA concentration is the sole factor contributing to the change in CFT. When considering all samples as a whole, the difference in CFT among the 3.7%, 4.2%, and 2.5–7.5g samples is also statistically significant, which suggests that the variance in CFT over both groups can be attributed to differences in PMMA concentration.

3.5 Conclusion

The results presented in this chapter demonstrate that it is possible to fabricate microporous PMMA membranes via a TIPS–air casting process. For a TIPS-air casting process, the design of the lacquer solution is of critical importance. As polymer nucleation and subsequent membrane formation are reliant on phase separation induced by a decrease in temperature, careful consideration of the solvent and non-solvent is required. The solvent needs to be volatile, while the non-solvent must have a higher boiling point in order to act as a porogen after polymer precipitation has occurred. We have shown that a mixture of acetone, ethanol, and butanol can meet these goals for PMMA, and leads to highly porous, integrally skinned asymmetric membranes.

Furthermore, we demonstrated that membrane morphology can be altered by varying the polymer loading of the lacquer. This alteration in morphology can lead to a number of changes. In addition, an increase in polymer loading led to a decrease in pore volume and an increase in the variation of the pore size distribution. The change in pore size distribution also played a role in the increase in surface area with respect to the increase in polymer loading; the formation of nanopores in samples with higher polymer loading is the reason for this increase. The last significant finding was the increase in CFT as the polymer loading increased; this was verified through ANOVA and t-test statistical analyses, which confirmed that the differences in CFT in relation to the PMMA concentration were statistically significant. This can probably be attributed to the increased skinning observed combined with the higher variation in pore size distribution, both of which can limit solvent access to the pore network and in turn restricts capillary flow in membranes.

While membranes were successfully cast and characterised, there are still issues that need to be resolved. In particular, delamination from the Melinex substrate and the brittleness of the

membranes warrant further investigation. One approach to address these issues would be membrane plasticisation, which is investigated in Chapter 5.

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Chapter 4

Probing the dual nature of the effect of water on pore formation in PMMA membranes

Abstract

This chapter describes the effect of humidity and water content on pore formation in PMMA membranes. Both the humidity in the casting chamber and the water content in the casting lacquer had an influence on pore morphology. Higher humidity led to an increase in pore volume and a decrease in the average pore size. When the relative humidity increased from 11.5% to 52.5%, the average pore size decreased from 1.5 to 0.64 μm . A greater proportion of skinning was observed in membranes cast at higher humidity, with skin layer coverage increasing from ~75% to 91.67%. Similarly, the surface area drastically increased from 6.8 to 30.5 $\text{m}^2 \text{g}^{-1}$ over the above humidity range. Most significantly, CFT also increased from ~210s to ~965 s as the humidity was increased. Differences in CFT as a function of humidity were statistically significant.

Water addition to the lacquer broadened the membrane PSD and at lower addition levels increased the average pore size while only slightly decreasing it at higher levels. The average pore size was 1.50 μm without water and ranged from 1.45 to 1.99 μm for membranes cast from samples with water. Skinning initially decreased and then increased with increasing water content in the lacquer. Membrane skin coverage was 84.7% without water and ranged 52.47% to 91.8% for samples containing water. Similarly, the surface area increased from 6.9 $\text{m}^2 \text{g}^{-1}$ to 10.8–11.3 $\text{m}^2 \text{g}^{-1}$. The above factors contributed to a change in CFT from 217 s for samples with no water to 202.7–302.7 s for samples including water. Differences in CFT as a result of water inclusion in the lacquer were statistically significant.

4.1 Introduction

This chapter describes experiments carried out to investigate the relationship between humidity and pore development in PMMA membranes. During the development of the process outlined in Chapter 3, it was noted that the CFT differed when membranes were cast at higher humidity levels. Therefore, further experiments were carried out to investigate the effect of adding water to the lacquer on membrane morphology, water inclusion was studied as it is often included as a constituent in other lacquers and can act as a porogen in the case of NC membranes as well as other VIPS systems [1].

4.2 Materials and methods

4.2.1 Materials

PMMA was obtained from Arkema (Altuglas[®] BS572). Acetone (HPLC grade, $\geq 99.5\%$) was purchased from Honeywell. Butanol (HPLC grade, $\geq 99.7\%$) was purchased from Sigma Aldrich and ethanol (HPLC grade, $\geq 99.9\%$) was purchased from Fischer Scientific. Polyester backing (Melinex 401, 75 μm in thickness) with a slip surface on one side was purchased from Teijin Films. Sodium dodecylbenzene sulfonate (SDBS, technical grade) was purchased from Sigma Aldrich. Deionised water was purchased from Fischer Scientific.

4.2.2 PMMA pre-drying

PMMA was dried before lacquer formulation as outlined in Chapter 3.

4.2.3 Lacquer formulation

Solvent blends were formulated using the ratios shown in **Table 4.1**. Solvents were weighed into a 250-mL Duran jar using a Fischer Scientific model PSS6001 analytical balance. After each addition, the balance was set to zero and the lid on the jar was secured. Solvents were added in the order of least to most volatile (butanol, ethanol, acetone). When all three solvents had been added, a magnetic stirring bar (40 mm $\times$ 0.5 mm) was added to the jar, which was then sealed and placed on an IKA RET hotplate held at 40 °C with the magnetic stirrer set to 600 RPM. The solvent mix was allowed to stir for 1 h to ensure homogeneity. Then samples of PMMA previously dried in a Memmert UN55 oven at 60 °C for a minimum of 72 h were added to the solvent mix and the Duran jar was placed back on the hotplate to allow the PMMA to fully dissolve under stirring for 24 h. To prepare samples containing

added water, after the 24 h stirring period the Duran jar was removed from the hotplate and the appropriate mass of water was added. The jar was then replaced on the hotplate and allowed to stir until any cloudiness disappeared.

Table 4.1: Composition of the lacquers used for water addition experiments.

Sample	Lacquer composition (g)				
	PMMA	Acetone	Butanol	Ethanol	Water
A	4.2	40.6	27.6	27.6	0
B	2.5	42.4	28.8	28.8	0
C	5	42.4	28.8	28.8	0
D	7.5	42.4	28.8	28.8	0
E	10	42.4	28.8	28.8	0
F	4.2	40.6	27.6	27.6	1
G	4.2	40.6	27.6	27.6	3
H	4.2	40.6	27.6	27.6	5

4.2.4 Membrane fabrication

Membranes were fabricated via TIPS–air casting using the apparatus described in Chapter 2. **Figure 4.1** shows a general schematic and the configurations for supplying desiccant, mixed, and humidified air to the apparatus.

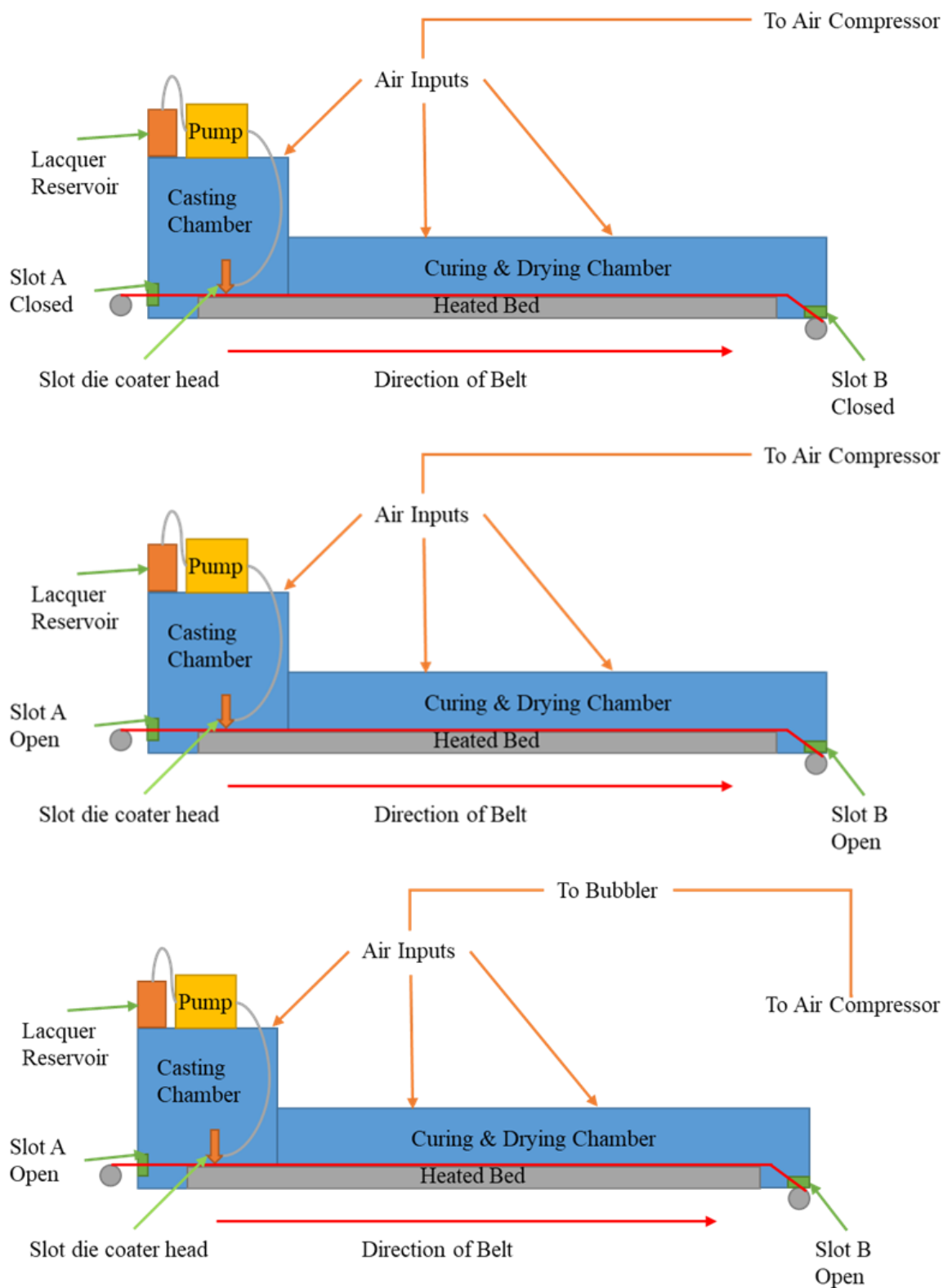


Figure 4.1: Diagram of the apparatus set-up for delivery of desiccant air (top), mixed air (middle), and humidified air (bottom).

4.2.5.1 Desiccant air casting

Desiccant air was supplied by a Kaeser AIRCENTER SX3 compressor and pumped into the casting and curing/drying chambers at a rate of 50 L min⁻¹ and a pressure of 1 bar before lacquer deposition. The air delivered to the curing and drying chambers was heated to 27 °C using a series of heated coils and a PID controller to monitor and control the temperature. The chambers were allowed to equilibrate for 20 min before lacquer deposition. Immediately before lacquer deposition, the air supply to the casting chamber was closed and the belt and the pump were switched on. The lacquer was then pumped through a slot die-coater head (FOM Technologies) with a spacer width of 200 µm onto a polyester backing drawn across a heated bed held at 27 °C. Following deposition, the polyester backing was cut at either end and both the entrance and exit slots were sealed (**Figure 4.1**), resulting in relative humidity (RH) of 11.5–14%. The membranes were sealed in the curing and drying chambers for 1 h and the air temperature was increased according to the schedule in **Table 4.2**. After 1 h had elapsed, the membrane was removed from the chamber, cut into three sections (start, middle, and end of the run) of approximately 30 cm in length, and then placed in a tray containing 1 L of tap water to remove any unevaporated solvents from the membrane matrix.

Table 4.2: Air temperatures and elapsed time for the membrane preparation process.

Air temperature (°C)	Time elapsed (min)
27	0
43	10
41	20
48	30
55	40
60	50

4.2.5.2 Mixed air casting

Desiccant air was supplied by a Kaeser AIRCENTER SX3 compressor and pumped into the casting and curing/drying chambers at a rate of 50 L min^{-1} and a pressure of 1 bar before lacquer deposition. The air delivered to the curing and drying chambers was heated to 27°C using a series of heated coils and a PID controller to monitor and control the temperature. The chambers were allowed to equilibrate for 20 min before lacquer deposition. Immediately before lacquer deposition, the air supply to the casting chamber was closed and the belt and the pump were switched on. The lacquer was then pumped through a slot die-coater head (FOM Technologies) with a spacer width of $200 \mu\text{m}$ onto a polyester backing drawn across a heated bed held at 27°C . Following deposition, both the entrance and exit slots were left open (**Figure 4.1**), resulting in RH of 23.5–25%. The membranes were allowed to sit in the curing and drying chambers for 1 h and the air temperature was increased according to the schedule in **Table 4.2**. After 1 h had elapsed, the membrane was removed from the chamber, cut into three sections (start, middle, and end of the run) of approximately 30 cm in length, and then placed in a tray containing 1 L of tap water to remove any unevaporated solvents from the membrane matrix.

4.2.5.3 Humidified air casting

To introduce humidified air, the air supply to the apparatus was disconnected and attached to a bubbler system with a sparging head as shown in **Figure 4.2**.

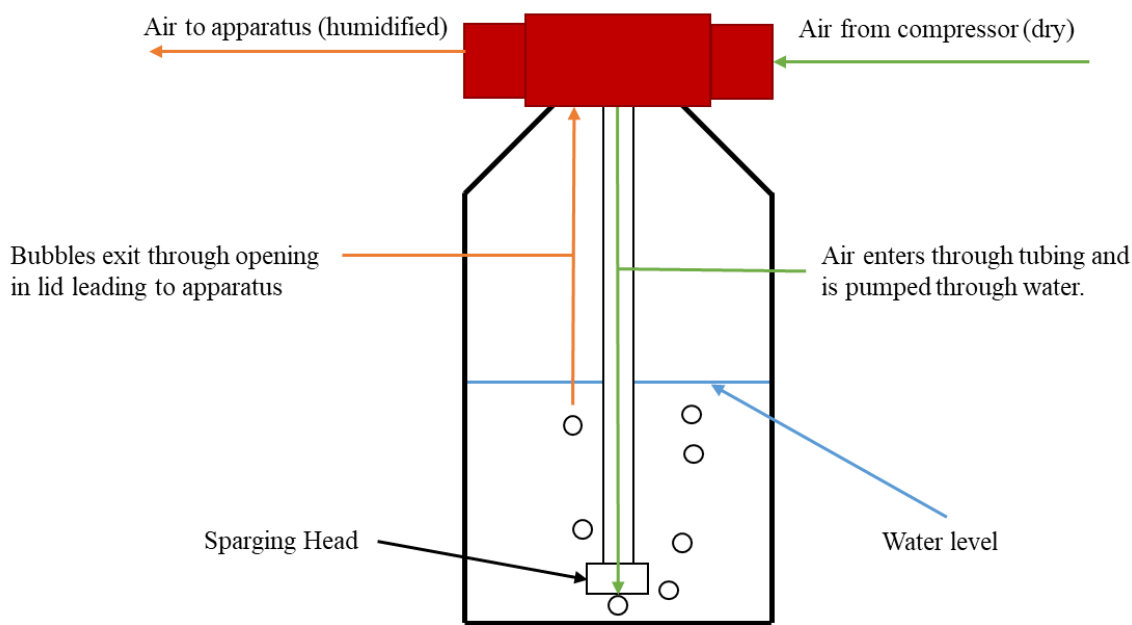


Figure 4.2: Bubbler set-up for delivery of humid air.

The bubbler was placed on an IKA RET hotplate held at 90 °C and the air supply was switched on. Air was supplied by a Kaeser AIRCENTER SX3 compressor at a pressure of 1 bar; a flow rate of $\sim 45 \text{ L min}^{-1}$ was observed after passing through the bubbler system. The air delivered to the curing and drying chambers was heated to 27 °C using a series of heated coils and a PID controller to monitor and control the temperature. The chambers were allowed to equilibrate for 20 min before lacquer deposition. Immediately before lacquer deposition, the air supply to the casting chamber was closed and the belt and the pump were switched on. The lacquer was then pumped through a slot die-coater head (FOM Technologies) with a spacer width of 200 μm onto a polyester backing drawn across a heated

bed held at 27 °C. Following deposition, both the entrance and exit slots were left open (**Figure 4.1**), resulting in RH of 45.4–52.5%. The membranes were allowed to sit in the curing and drying chambers for 1 h and the air temperature was increased according to the schedule in **Table 4.2**. After 1 h had elapsed, the membrane was removed from the chamber, cut into three sections (start, middle, and end of the run) of approximately 30 cm in length, and then placed in a tray containing 1 L of tap water to remove any unevaporated solvents from the membrane matrix.

4.3 Membrane characterisation

4.3.1 Lacquer characterisation

Lacquers were characterised by measuring the turbidity using a Lovibond TB 100 tintometer during sample cooling, as described in detail in Chapter 3.

4.3.2 Water titrations

Water titrations were carried out to determine the point at which water in the lacquer changes from acting as a solvent to acting as a non-solvent. Lacquer samples of 100 g containing 2.5–10 g of PMMA or 4.2% PMMA were formulated in 250-mL Duran solvent jars as outlined in Chapter 3.

Samples were placed on an IKA RET hotplate held at 35 °C with a stirring speed of 250 RPM. Water was added in 1-mL increments by first turning off the magnetic stirrer, then removing the lid on the jar. After the water was added, the lid was replaced and the stirrer switched on; the next 1-mL aliquot of water was added when any nucleation or cloudiness in the solution had disappeared. Water was added until the cloudiness persisted at 35 °C. All samples were run in triplicate.

4.3.3 SEM imaging

Images of the skin (the open side of the membrane that faces into the air) and belt layers (the closed side of the membrane facing the Melinex) as well as cross-sections of the membrane samples were imaged using a Zeiss Ultra SEM instrument with a Gemini electron optical column and an acceleration voltage of 2.5 keV. Further details are provided in Chapter 3.

4.3.4 Capillary flow time

Samples of the membranes were cut into strips of 4 cm × 1.5 cm across the web from the middle of the cast run and the centre of the membrane, ensuring that the backing remained on the sample. CFT measurements were then carried out and statistical analysis was conducted as described in Chapter 3.

4.3.5 BET analysis

BET analysis was performed using a Nova 2400e surface area and pore size analyser (Quantachrome). Before analysis, samples were degassed in an oven at 100 °C for 1 h.

4.3.6 Mercury porosimetry

Mercury porosimetry was performed using an Autoscan-33 porosimeter (Quantachrome) and the pore diameter was then calculated for each membrane sample. Further details are described in Chapter 3.

4.3.7 ImageJ SEM analysis

Analysis of SEM images was performed using ImageJ as described in Chapter 3.

4.4 Results and discussion

4.4.1 Lacquer characterisation

Lacquers were characterised by measuring the turbidity as a function of temperature. The results are presented in **Figure 4.3**. Data generated from the experiments described in Chapter 3 for the 4.2% lacquer solution were used for comparison and to determine the effect of added water on the cloud point.

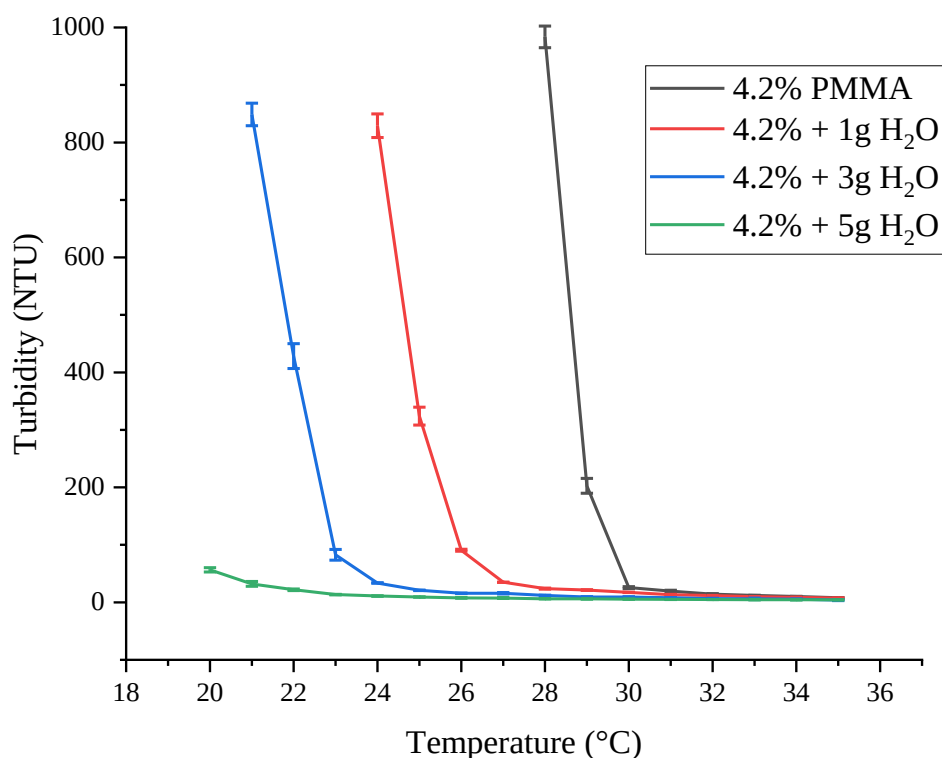


Figure 4.3: Graph of turbidity versus temperature for 4.2% PMMA lacquers with and without added water.

The results in **Figure 4.3** show that the cloud point decreased with increasing water addition. The samples containing 0, 1, and 3 g of water had a distinct inflection point in the turbidity curve (i.e. cloud point) at 29 °C, 26 °C, and 23 °C, respectively. For the sample with 5 g of

water, a slight inflection point in the turbidity curve is evident between 22 °C and 20 °C, but no distinct cloud point was observed as for the other three samples.

The overall trend indicates that the PMMA solubility increased with the water concentration; in other words, PMMA is more likely to dissolve at a lower temperature. This is in contrast to what Flory–Huggins solution theory and the Hansen solubility parameters described in Chapter 1 would suggest. **Figure 4.4** shows the proximity of water to PMMA when plotted in Hansen space [2]. Hansen space is generated by treating the Hansen solubility parameters as X, Y and Z co-ordinates in a 3D plot. Solvents are assigned a radius of 1, while the interaction parameter for a polymer acts as its radius in the Hansen plot [2,3]. Any solvent within the radius of the polymer’s interaction parameter can be considered a good solvent, while any solvent outside this radius is considered a poor solvent or a non-solvent. It would be expected that water would act as a non-solvent because of its location outside the interaction radius of PMMA in **Figure 4.4**.

Table 4.3 shows approximations of the Flory–Huggins parameter χ as a function of water added to the lacquer. As more water is added, χ tends towards 1, which in theory should lead to a solution in which PMMA is non-soluble [3], but this was not the case. Using these assumptions, the cloud point should shift above the 29 °C observed for a lacquer containing no water, but lower cloud points were observed. This anomaly can possibly be explained by work carried out by Hoogenboom et al. on the solubility of PMMA in water–ethanol mixes [4,5]. Hoogenboom et al. reported that the increase in solubility is due to the formation of hydrogen bonds between water and the ester group on PMMA side chains. This allows the PMMA chains to become hydrated and detangle as neighbouring ester–water-bound monomer segments, while a water “shell” that acts as a compatibilising layer between water and the polymer is also formed [4,5]. However, as outlined in Chapter 3, as the enthalpy of the system decreases, the entropy of the system tends towards agglomeration, possibly because water–ethanol hydrogen bonding is favoured over ester–water hydrogen bonding

when the temperature drops below a certain threshold. This unexpected water relationship is important in air casting because water from the ambient air can adsorb onto the membrane, increasing solubility near the surface.

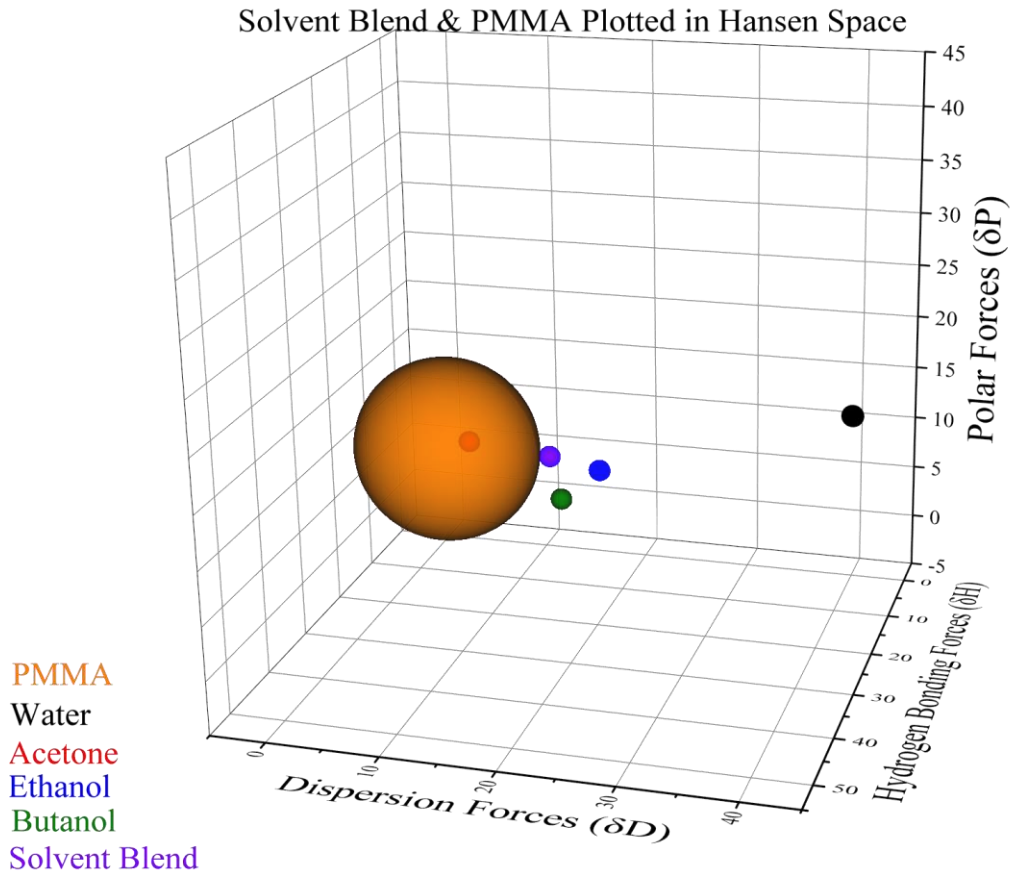


Figure 4.4: PMMA interaction radius with lacquer components plotted in Hansen space [3].

The Flory–Huggins parameter χ was approximated using a Hansen-based approach according to the following equation [6]:

$$\chi = \frac{V_m}{RT \times (\delta_{d2} - \delta_{d1})^2 + 0.25(\delta_{p2} - \delta_{p1})^2 + 0.25(\delta_{h2} - \delta_{h1})^2}, \quad (1)$$

where:

δ_d is the dispersive force between molecules (1 denotes solvent, 2 denotes polymer);

δ_p is dipole interactions (1 denotes solvent, 2 denotes polymer);

δ_h is the hydrogen bonding contribution (1 denotes solvent, 2 denotes polymer);

V_m is the molar volume of the solvent measured at 25 °C;

R is the universal gas constant; and

T is the absolute temperature in Kelvin.

As the samples contained multiple solvent/non-solvent components, the contributions to δ_d , δ_p , and δ_h were taken as a fraction of the total solution composition for each one. As a working example for 0 g of added water, the following values were calculated for the contributions from acetone (accounting for 42.3% of the lacquer composition):

$\delta_d = 15.5$ [3], so the acetone δ_d contribution is $15.5 \times 0.423 = 6.56$

$\delta_p = 10.4$ [3], so the acetone δ_p contribution is $10.4 \times 0.423 = 4.4$

$\delta_h = 7$ [3], so the acetone δ_h contribution is $7 \times 0.423 = 2.96$

$V_m = 74$ [3], so the acetone V_m contribution is $74 \times 0.423 = 31.32$

The contributions were then calculated for each component in the lacquer. When summed, the total contributions give an approximation of the Hansen parameter [3]. **Table 4.4** lists values of δ_d , δ_p , δ_h , and V_m calculated from the summed contributions for the solvent mix, and δ_d , δ_p , and δ_h values for PMMA [3].

Table 4.3: Hansen solubility parameters for the solvent mix and PMMA.

	δ_d	δ_p	δ_h	V_m
Solvent mix	15.73	8.58	13.11	74.57
PMMA	18.5 [3]	10.5 [3]	5.7 [3]	—

Then **Equation (1)** can be used to approximate χ , given $R = 8.31446$ and $T = 298.15$ K:

$$\chi = \frac{74.57}{(8.31446)(298.15) \times (18.5 - 15.73)^2 + 0.25(10.5 - 8.58)^2 + 0.25(5.7 - 13.11)^2} = 0.67$$

Approximations for water additions of up to 5 g were calculated using this method and are listed in **Table 4.4**.

Table 4.4: Approximation of χ for lacquers with added water using fractional Hansen solubility parameters.

Water added (ml)	0	1	2	3	4	5
χ value at 25 °C	0.67	0.7	0.73	0.75	0.78	0.81

4.4.2 Water titrations

Water titrations were carried out to determine the point at which water in the lacquer changes from acting as a solvent to acting as a non-solvent. The method used was a variation of a widely used approach, as mentioned by Lin et al. [7] and Wijmans et al. [8] and outlined by Mulder [9]; the modification involved using a static measurement temperature of 35 °C. This temperature was chosen as it was above the cloud point for each sample and all the solutions were thermodynamically stable, resulting in a transparent solution (**Figure 4.3**). Therefore, water titrations were carried out at 35 °C. To determine if PMMA loading played any significant role in changes to turbidity with respect to the quantity of water added, samples with 2.5 g, 5 g, 7.5 g, and 10 g of PMMA were tested alongside the 4.2% PMMA lacquer. The results are presented in **Table 4.5**.

Table 4.5: Titration values for lacquer samples containing 2.5, 5, 7.5, and 10 g of PMMA and 4.2% PMMA.

Sample	Titre (ml)			
	1	2	3	Mean
2.5 g PMMA	35	34	35	34.66
5 g PMMA	34	33	33	33.33
7.5 g PMMA	33	34	33	33.33
10 g PMMA	33	34	33	33.33
4.2% PMMA	35	34	33	34

After addition of water, a slight phase separation was observed at the point of lacquer–water contact. This resulted in the formation of white PMMA agglomerates after small additions, while more densely packed translucent gels were observed when higher amounts of water were added. These agglomerates and gels subsequently ‘dissolved’ and the lacquer returned to a transparent state after stirring for times ranging from several minutes (<10 mL added) to more than 1 hour (>25 mL added). Note, the term ‘dissolve’ is widely used but whether the polymer is truly dissolved as a unimer is unknown. In addition, the PMMA loading played a role in the persistence of these structures: samples with 2.5 g of PMMA showed faster dissolution in comparison to those with 10 g of PMMA. This can be attributed to the greater enthalpy required to fully detangle the agglomerate and a similar transition as highlighted in Chapter 3, whereby as the lacquer phase separation a transition from a clear to a cloudy to a gelated state occurs. In part, this phenomenon may be explained by critical solution theory and specifically the upper critical solution temperature, as shown in **Figure 4.5**. When the water is initially added, as it is added at room temperature there will be a net drop in temperature in the system and the solution will cross the binodal line into the metastable region, which induces an initial nucleation and growth phase that results in

agglomeration of the polymer [7,10]. After heating to 35 °C the solution crosses back over the binodal curve and tends towards a single phase, leading to dissolution of the PMMA and the disappearance of the agglomerates.

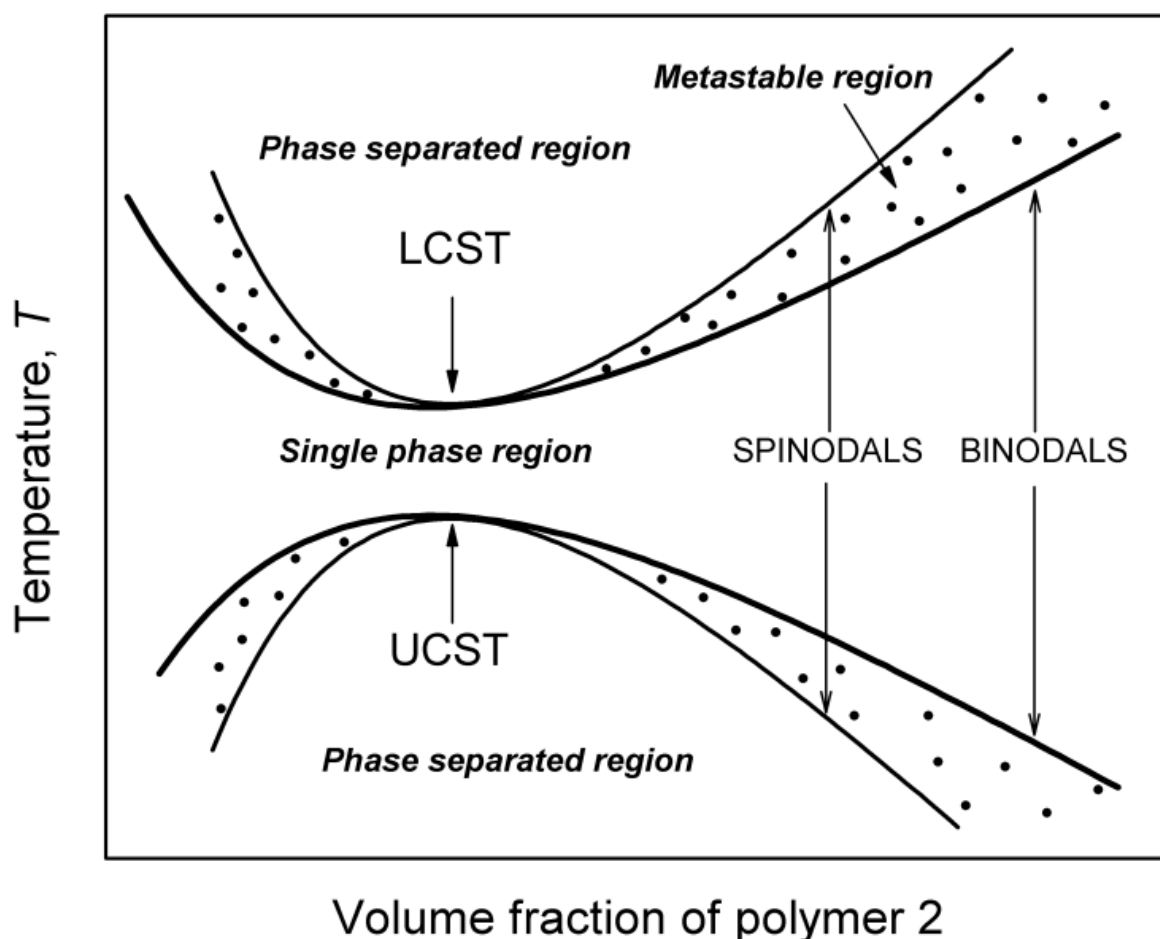


Figure 4.5 Diagram showing the upper and lower critical solution temperatures along with binodal and spinodal lines [11].

From the results obtained for titrations and as outlined in Section 4.1, while PMMA acts as a non-solvent according to the Hansen parameters and interactions, it is in fact more soluble in water–alcohol mixes than expected. This cannot be attributed to a single factor and is most likely because of a combination of the change in χ as the solvent mix is loaded with more water (**Table 4.4**) and the interaction between water and PMMA leading to the formation of a water shell surrounding the polymer, as outlined by Hoogenboom et al. [4,5] and

highlighted in the previous section. Furthermore, as variable PMMA loading was tested and no significant change in the amount of water required to induce turbidity was observed, it is highly likely that at a given temperature the turbidity is determined by the solvent/non-solvent composition and is independent of the PMMA loading.

4.4.3 Membrane appearance

Membranes cast at low, medium, and high humidity exhibited similar delamination and brittleness as seen for the 4.2% PMMA samples discussed in Chapter 3. There was no discernible difference in the degree of delamination or brittleness. All the samples showed delamination at the edges of the membrane which was also observed for 3.7 and 4.2% samples discussed in Chapter 3. When removed from the backing the membranes were seen to be flexible but quite flimsy and brittle and when force was applied, they tore easily, as for the 3.7% and 4.2% PMMA samples discussed in Chapter 3. All samples were matte white and opaque in appearance, similar to the 3.7% and 4.2% PMMA samples discussed in Chapter 3.

These samples appear to be quite similar in appearance to the 3.7% and 4.2% PMMA samples discussed in Chapter 3. This is as expected, as the same lacquer composition as for the 4.2% PMMA samples was used, with humidity the only variable in this series of experiments. As the only difference is the humidity, which will affect the evaporation rate for the solvents [12–14], it is expected that the physical appearance would be similar to that of the samples discussed in Chapter 3.

The matte appearance of the membranes is due to the amorphous nature of PMMA and the random packing of polymer chains [15].

The samples with added water exhibited greater delamination compared to samples cast with no water added. The greater the water addition, the greater was the delamination observed.

Similar to samples with no water added, delamination seemed to originate at the edges and move towards the centre of the membrane. In one area of the 5g sample, an entire region delaminated. These membranes were less flexible than samples with no water added and exhibited similar tearing when force was applied. In the case of membranes with 5g of added water, when sufficient force was applied the membrane tore and became powder-like. All samples were matte white and opaque in appearance.

The greater delamination may be attributed to interaction of the water included in the lacquer and the “slip” surface on the polyester backing. As the delamination increased with increasing water content in the lacquer, it is reasonable to assume that the slip agent on the surface is hydrophobic, resulting in less binding to the surface. However, as previously mentioned, the exact nature of the slip agent is unknown for commercial sensitivity reasons. Therefore, without knowing the exact nature of the slip agent, any conclusions on delamination remain speculative.

The brittleness of the membranes can in part be attributed to the glass transition temperature of PMMA [16,17]. However, as discussed in Sections 4.4.1 and 4.4.2, the addition of water fundamentally changes the way PMMA phase separates and thus alters the subsequent membrane morphology. The resulting change in pore morphology may in turn contribute to membrane brittleness.

The matte appearance can be accredited to the amorphous nature of PMMA and random packing of polymer chains [15].

4.4.4 SEM imaging

Figure 4.6 shows SEM images obtained for 4.2% PMMA membranes cast at low, medium, and high humidity.

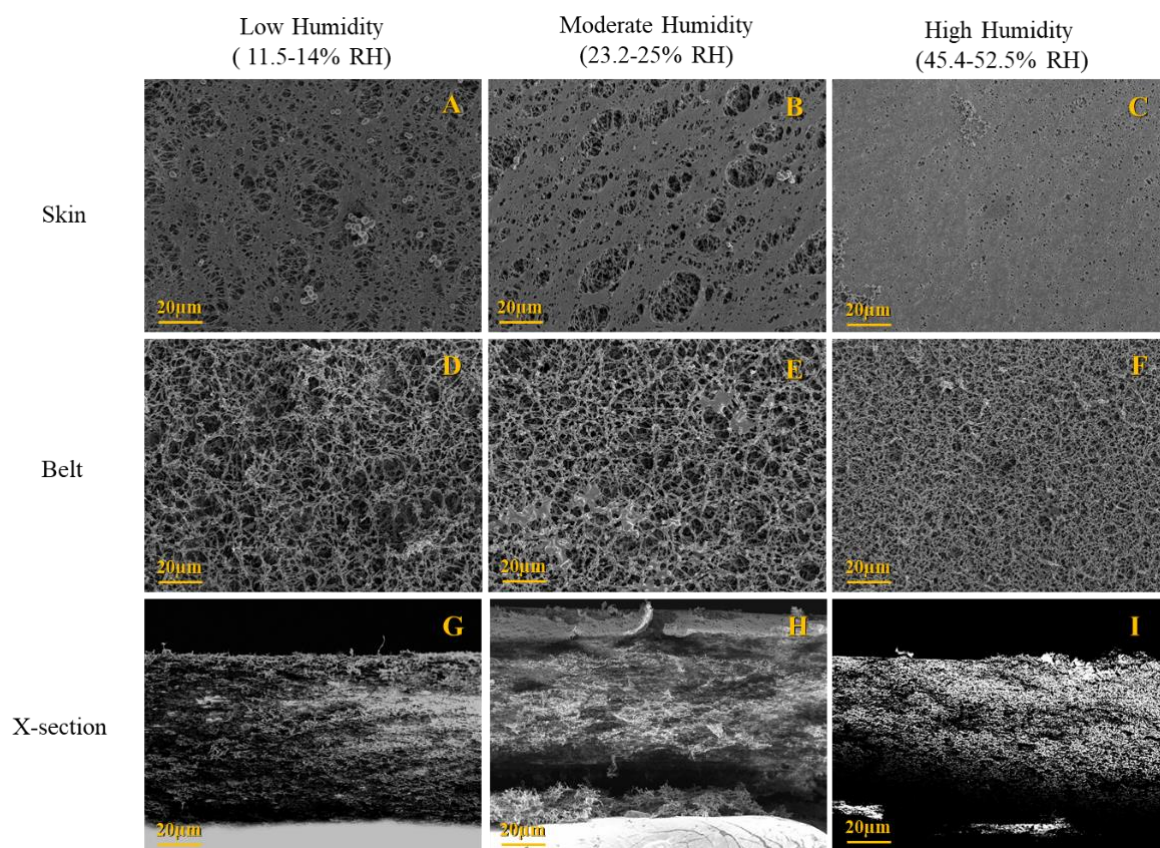


Figure 4.6: SEM images of skin and belt layers and cross-sections of PMMA membranes cast at low, medium, and high humidity.

For the skin layers of the membranes, progressive skinning is observed going from low to medium to high humidity, which may be explained by the solvent uptake capacity of the air. Air of lower humidity will have a greater capacity to remove solvent as it is not saturated with water vapour. By contrast, air at medium and high humidity led to membranes with increased skinning because of lower ability to carry away solvent as it evaporates. This

results in slower solvent evaporation and migration of more PMMA towards the air side of the membrane as it cures and the solvent evaporates [18].

In the case of the belt layers, the pore density appears to increase when going from low to medium to high humidity, which may again be explained by the solvent removal capacity of the air in the chamber. At higher uptake capacity, solvent can evaporate at a faster rate, which in turn decreases the solvent migration time through the gel network formed as the lacquer phase separates. As the humidity increases the uptake capacity of the air decreases [12,19], reducing surface evaporation at the skin side of the membrane. This increase in evaporation time leads to a smaller average size for droplets evaporating from the air side of the membrane, which may explain the smaller, denser pore structures seen for the higher-humidity conditions. There is also some evidence from cross-sectional images of the three samples. The average pore size appears to decrease, with pores more densely packed in cross-section images of the medium- and high-humidity samples. The pore density in the bulk combined with the skinned top layer and more porous belt layer means that the membranes produced can be classed as asymmetric [20].

Figure 4.7 shows membranes samples cast with 1, 3, and 5 g of water added to stock 100-g samples of 4.2% PMMA lacquer solution.

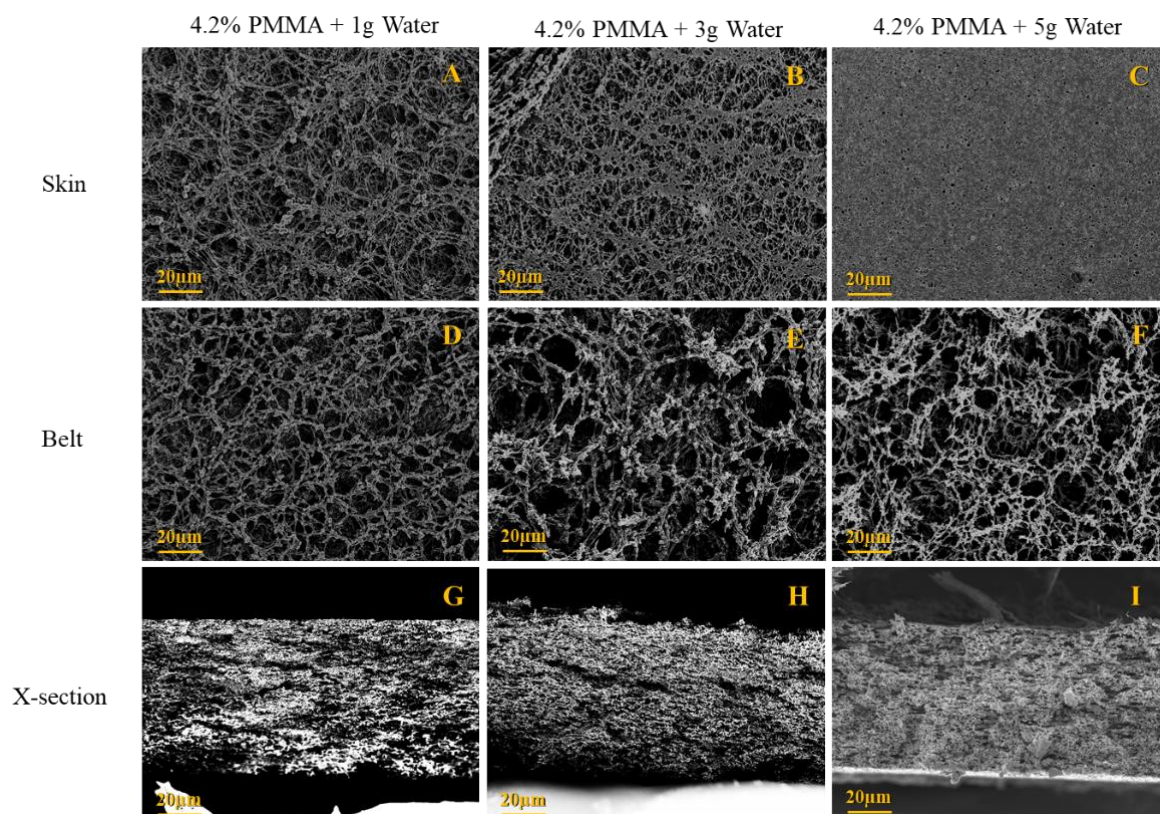


Figure 4.7: SEM images of skin and belt layers and cross-sections of membranes cast from 4.2% PMMA lacquers with 1, 3, and 5 g of added water.

Inspection of the skin layers reveals increased skinning with increasing water content. There is little to no skinning for the membrane cast from lacquer with 1 g of added water, which may be explained by the higher PMMA solubility compared to the 4.2% PMMA lacquer with no added water. When added at low volumes, water may allow greater interaction with butanol and ethanol through the formation of water cages around the PMMA chains [4,5], delaying total phase separation, as ethanol and butanol can now act as solvents below the cloud point of the lacquer. In addition, water will form an azeotrope when mixed with either

ethanol or butanol [21], which may alter the order in which the solvents evaporate and give rise to regions where azeotrope and pure-component zones may coexist.

When the water content was increased, an increase in skinning was observed; while water cages may be present around the PMMA chains, the likelihood of an azeotropic effect increases as the ratio of water to PMMA increases from 4.2:1 (1 g) to 1.4:3 (3 g) to 1:5 (5 g). Thus, an increase in the water/PMMA ratio may lead to azeotropic regions in the gel formed when the lacquer phase separates, particularly in the case of the sample with 5 g of added water, as the mass of water is greater than the mass of PMMA in this lacquer. The formation of azeotropes means that there would be two additional temperatures at which non-solvents could evaporate: 78.1 °C for a water–ethanol azeotrope (ethanol boiling point 78.4 °C, water boiling point 100 °C) and 92.4 °C for a water–butanol azeotrope (butanol boiling point 117.8 °C, water boiling point 100 °C). In addition, the water itself may act as a non-solvent in this system, giving rise to a third porogen alongside ethanol and butanol.

In contrast to the skin layers, the belt layers shown in **Figure 4.7** appear to have an increasingly open structure as the water concentration is increased. This too may be attributable to the increase in PMMA solubility on addition of water. However, as mentioned for previous samples described in Chapter 3, the belt layer has a more open structure because of non-solvent migration towards the air interface [18], while the water shells may promote solvation on the belt side, allowing the generation of larger pores.

Cross-sectional images of the samples again show that the membranes produced are asymmetric and have a less porous skin layer (3 g and 5 g) and a more open skin layer, with pores also evident in the bulk membrane [20].

4.4.5 Mercury porosimetry

Figure 4.8 shows porograms for membranes cast at low, medium, and high humidity.

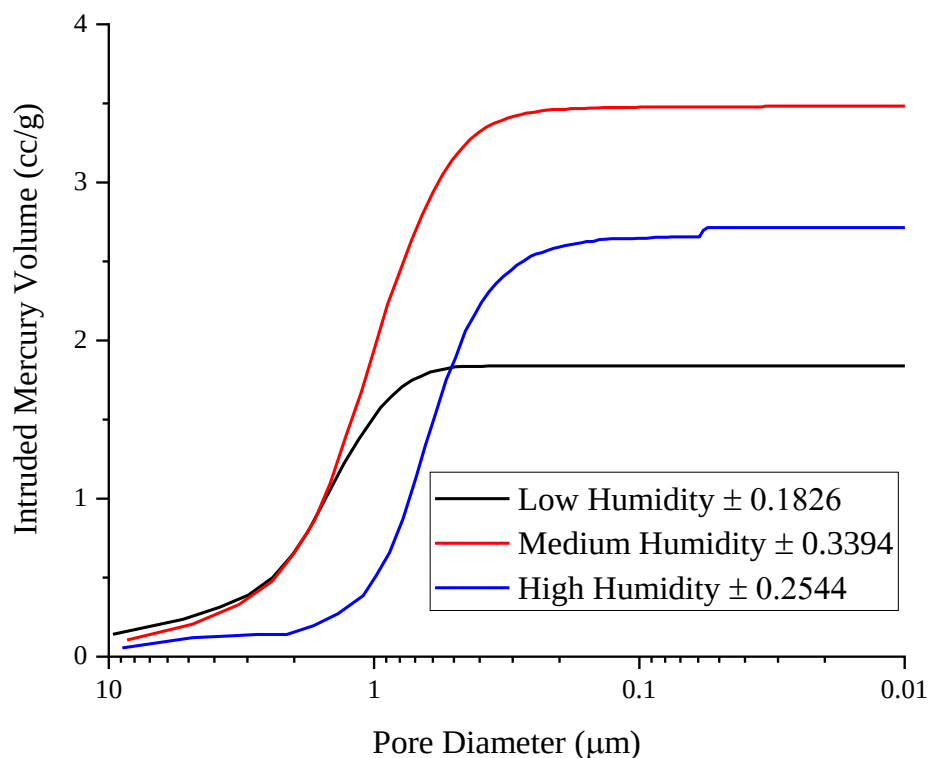


Figure 4.8: Porograms for 4.2% PMMA membrane samples cast at low, medium, and high humidity.

The results show an increase in pore volume when going from low to medium humidity, followed by a drop when going from medium to high humidity; however, the pore volume is greater for the high-humidity sample than for the low-humidity sample. This is most likely related to the evaporation rate, which was highlighted in the previous section. A reduced evaporation rate leads to the formation of smaller pores and a corresponding increase in pore volume [18].

The data show that the membrane cast at medium humidity has the greatest pore volume. This is most likely because of the broad range observed for the pore size, ranging from ~5

μm to $\sim 110\text{ nm}$, which will play a role in the overall pore volume. Interestingly, the pore morphology appears to fall between the morphologies observed for the low- and high-humidity samples, as it has both a significant microstructure and nanostructure, while the low- and high-humidity samples exhibit a predominantly microstructure and nanostructure, respectively.

Figure 4.9 shows the pore size distribution for membranes cast at low, medium, and high humidity.

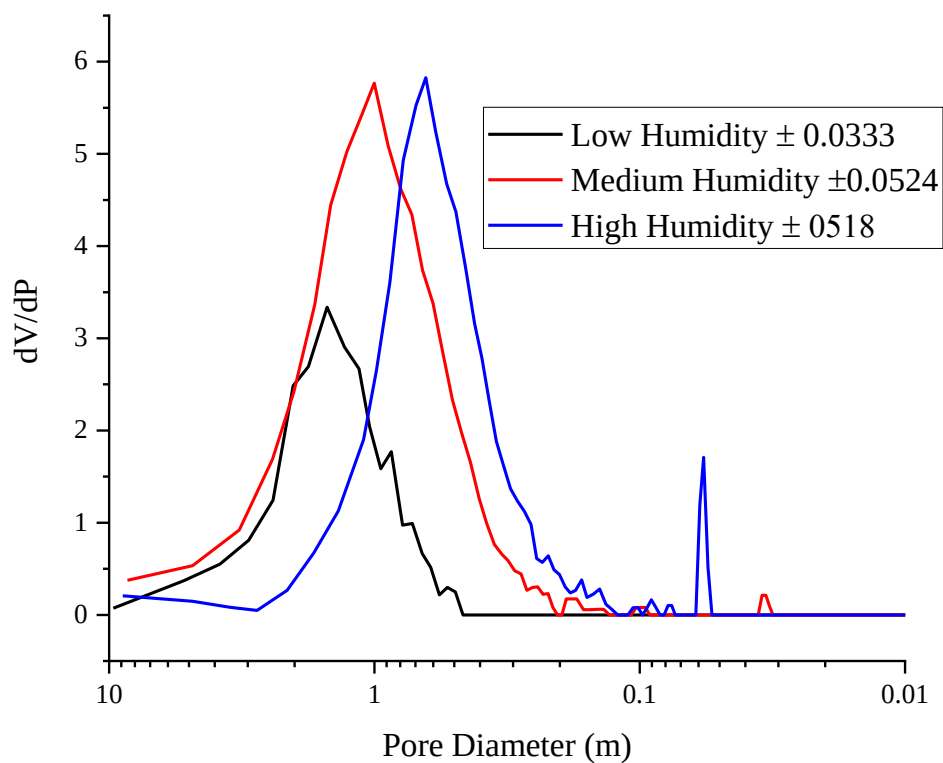


Figure 4.9: Pore size distribution for 4.2% PMMA membrane samples cast at low, medium, and high humidity.

The trends in **Figure 4.9** reveal that the average pore size decreased with increasing humidity. This is most prevalent for the high-humidity sample, for which the peak pore size is in the sub-micron region, with an additional peak in the nanometre region. The sample

cast at medium humidity shows a broader pore-size range stretching from the micrometre to the nanometre region, with a single peak appearing below 100 nm. In contrast to the medium- and high-humidity samples, the low-humidity sample has a narrower pore distribution, with no peaks observed below 500 nm. The average pore size was 1.5, 1.01, and 0.64 μm for low, medium, and high humidity samples, respectively.

The nanopores produced in the medium- and high-humidity samples can probably be attributed to suppression of solvent evaporation by the RH [12,13], resulting in the formation of smaller solvent droplets, and thus a smaller pore size on membrane curing. Furthermore, Fukatani et al. [14] showed that higher humidity alters the temperature of evaporating drops of ethanol. At lower humidity and high temperature (35% RH), individual drop temperatures were more uniform, while at higher humidity and temperature (90% RH) drops had a higher interfacial temperature and lower internal temperature, probably because of the heat of absorption, adsorption, or condensation of water from the vapour phase [14]. This variation in temperature will play a role in inhibiting solvent evaporation and thus affect the pore sizes observed in samples.

Figure 4.10 shows the pore volume for samples with 1, 3, and 5 g of water added in comparison to a sample containing no water.

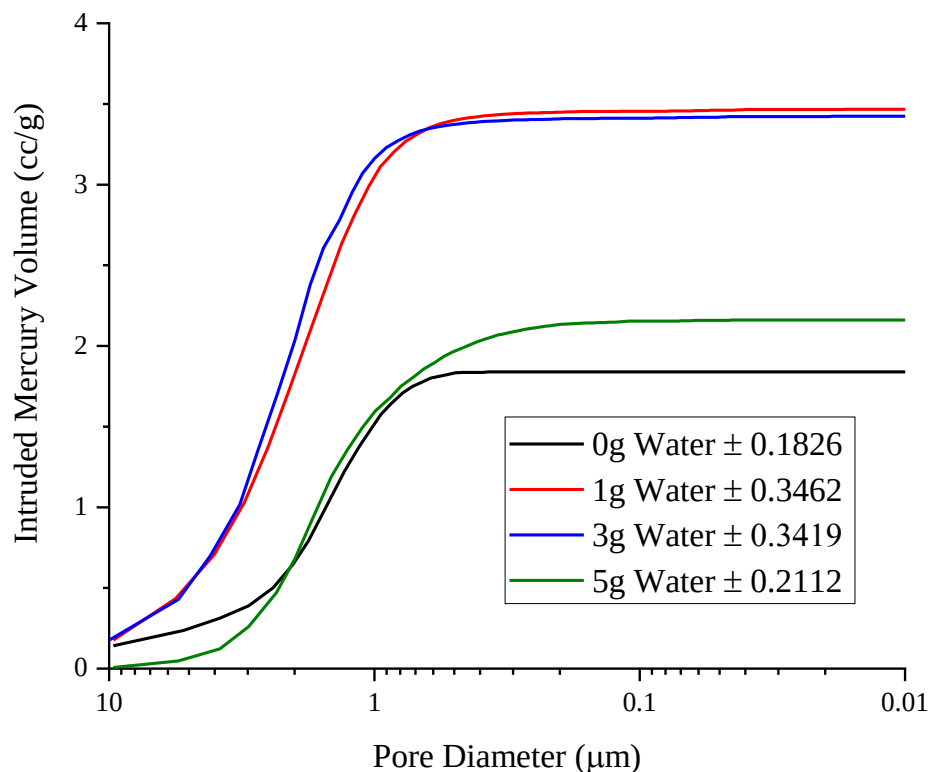


Figure 4.10: Porograms for 4.2% PMMA membrane samples cast with 0, 1, 3 and 5 g of water added.

In general, the pore volume increased with the water content, but decreased when the water content increased from 3 g to 5 g. The increase in pore volume may be explained by the presence of water and butanol–water and ethanol–water azeotrope mixtures, which would act as three extra porogen phases in the lacquer and may be responsible for the increasingly broad pore-size distribution shown in **Figure 4.11**. The increase in pore volume for samples with 1 g and 3 g of added water may be attributable to an increase in PMMA solubility due to PMMA–water interactions, while the decrease in pore volume observed when the added water was increased from 3 g to 5 g may be explained by a more dominant azeotropic effect, as the water loading is greater than the PMMA loading. In this case, the PMMA may be

saturated with the maximum number of water–PMMA interactions, allowing the excess water to interact with the ethanol and butanol in the lacquer and forming azeotrope phases that have different boiling points to those of pure ethanol, butanol, and water.

Figure 4.11 shows the pore size distribution for membranes cast with 1, 3, and 5 g of added water in comparison to a sample with no water.

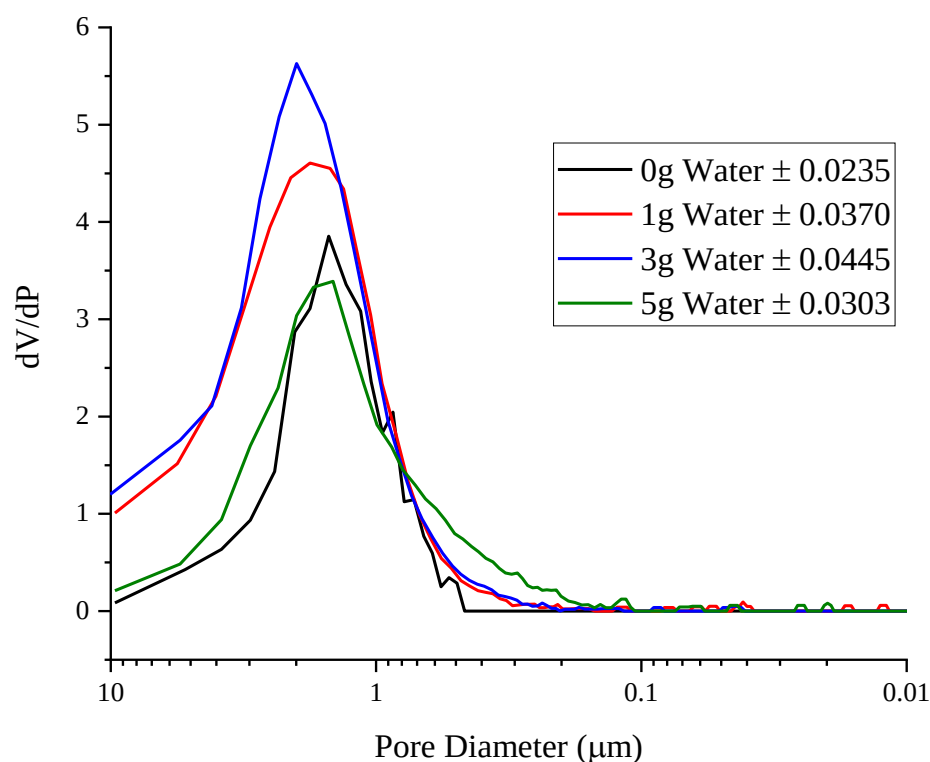


Figure 4.11: Pore size distribution for 4.2% PMMA membrane samples cast with 0, 1, 3 and 5 g of water added.

Changes in the pore size distribution with increasing water content are evident. In general, the pore distribution broadens as the water content increases when compared to a sample containing no water. The average pore size was 1.5, 1.77, 1.99, and 1.45 μm for water addition of 0, 1, 3, and 5 g, respectively.

4.4.6 BET data

BET data for samples cast at low, medium, and high humidity are shown in **Table 4.6**.

Table 4.6: Surface area generated from BET analysis for 4.2% PMMA membrane samples cast at low, medium, and high humidity.

Sample	Surface area ($\text{m}^2 \text{g}^{-1}$)
4.2% PMMA at low humidity	6.8 ± 0.21
4.2% PMMA at medium humidity	21.2 ± 0.57
4.2% PMMA at high humidity	30.5 ± 0.55

It is evident that the surface area increased with the humidity, which is consistent with the pore size distributions shown in **Figure 4.8**. The proportion of nanopores increased with the humidity, so the surface area would also be expected to increase. The drastic jump in surface area from 6.81 to $21.25 \text{ m}^2 \text{g}^{-1}$ when comparing the low- and medium-humidity samples is due to the decrease in mean pore size from ~ 1.5 to $\sim 1 \mu\text{m}$, while the more modest increase from 21.25 to $30.69 \text{ m}^2 \text{g}^{-1}$ when comparing the medium- and high-humidity samples can be attributed to the decrease in mean pore size in addition to the peak observed at $\sim 60 \text{ nm}$ in the pore size distribution.

BET data for samples cast from lacquers with added water are shown in **Table 4.7** in comparison to a sample with no added water.

Table 4.7: Surface area data generated through BET analysis for 4.2% PMMA membranes cast with 1, 3, and 5 g of water added.

Sample	Surface area ($\text{m}^2 \text{g}^{-1}$)
4.2% PMMA	6.9 ± 0.08
4.2% PMMA +1 g of water	11.1 ± 0.29
4.2% PMMA + 3 g of water	11.3 ± 0.29
4.2% PMMA +5 g of water	10.8 ± 0.29

The changes in surface area are as expected when the pore size distributions of the samples are taken into account. Samples cast from lacquer with added water showed an increase in pores around the 1- μm range, with numerous peaks observed in the submicron region. This in turn will increase surface area, as observed from the BET data. The difference between the 5 g sample and the 1 g and 3 g samples is most likely because of the lower number of particles in the 1- μm range, which appears to be approximately the same as for the sample containing no water. However, there is a large distribution of pores ranging from 0.1 to 1 μm that contribute to the increase in surface area compared to the sample with no water.

In general, it is evident that humidity has a greater effect on the variation in surface area because of its influence on evaporation of the solvents. By contrast, when water is added to the lacquer it forms new porogen phases that are readily drawn off under low-humidity conditions.

4.4.7 ImageJ SEM analysis

Results for skin coverage are presented in **Table 4.8** for samples cast at varying humidity and in **Table 4.9** for samples cast with added water. Corresponding histograms of pore sizes detected in these samples are presented in **Figure 4.12** and **Figure 4.13**, respectively. The SEM images presented in **Figures 4.6** and **4.7** were used for ImageJ analysis. As described in **Section 3.3.7**, the images were sharpened prior to analysis to allow easier detection of skin boundaries and defects in the skin layer during when processing the images to give greater accuracy in measuring the skin coverage.

Table 4.8: Percentage skin coverage for PMMA membrane samples cast at low, medium, and high humidity.

Sample	Skin layer coverage (%)
Low humidity	75.3
Medium humidity	78.84
High humidity	91.67

The results presented in **Table 4.8** show a trend whereby skin layer coverage increased with increasing humidity. These findings are as expected from the raw SEM images in **Figure 4.6**. This increase in skin coverage is a result of slower solvent evaporation as the membranes cure, which in turn leads to a greater abundance of PMMA that can migrate towards the air interface [18].

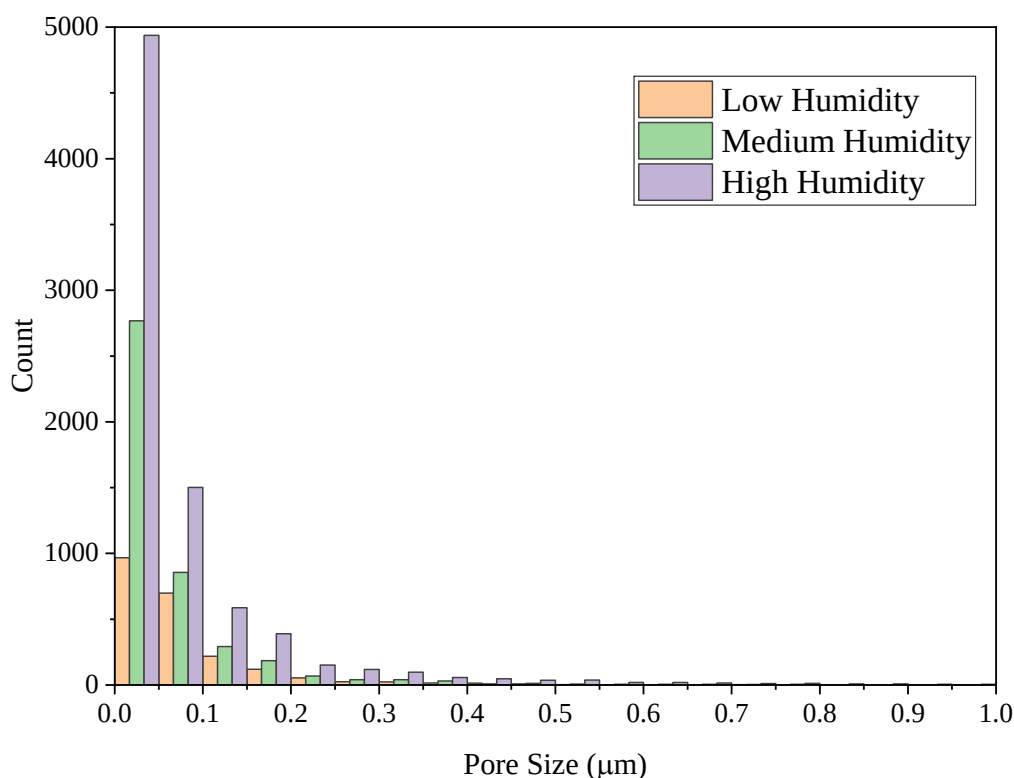


Figure 4.12: Histogram of pore sizes detected using ImageJ for membranes cast at low, medium, and high humidity.

The data presented in **Figure 4.12** show that an increase in humidity led to an increase in nanopore formation, in agreement with the mercury porosimetry data presented in **Figure 4.9**. In general, the pore size trend obtained using ImageJ is similar to the trend observed in **Figure 4.9**. For the sample cast at high humidity, the presence of a large volume of pores of <100 nm is in agreement with the large peak at 50–60 nm observed in **Figure 4.9**. In addition, the majority of the other peaks observed for the mercury porosimetry data in **Figure 4.9** correspond to the ImageJ analysis results for the SEM images. Similar to the increase in skin coverage, this trend for the formation of smaller pores with increasing humidity can be attributed to the decrease in the rate of solvent evaporation [12,13,18].

Table 4.9: Percentage skin coverage for PMMA membrane samples cast with and without water addition.

Sample	Skin layer coverage (%)
0g water	84.71
1g water	52.36
3g water	66.6
5g water	91.8

The data presented in **Table 4.9** show that the addition of 1 g of water to the PMMA lacquer led to a decrease in skin coverage from 84.71% to 52.36%. As the amount of water added was increased to 3 g and 5 g, the coverage then increased to 66.6% and 91.8%, respectively. The decrease can be attributed to greater interaction of PMMA with ethanol and potentially butanol due to the formation of water cages around PMMA [4,5]. The increase in skin coverage from 1 g to 3 g to 5 g is in accordance with the visual observations from **Figure 4.7**.

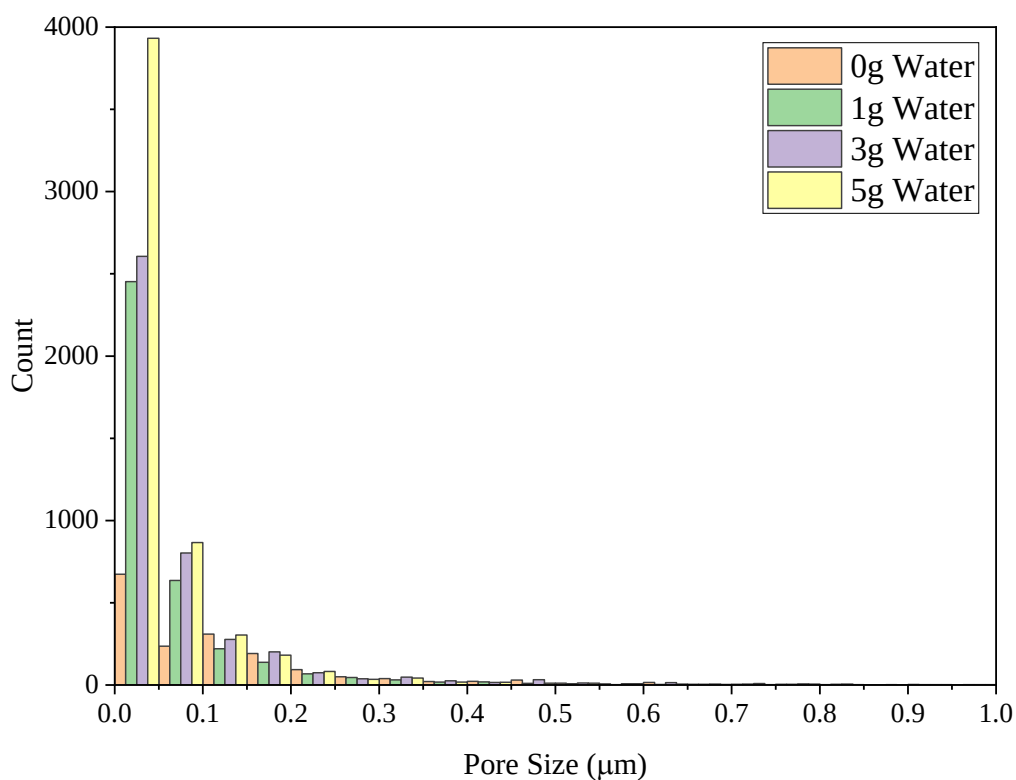


Figure 4.13: Histogram of pore sizes detected using ImageJ for membranes cast with 0, 1, 3, and 5 g of added water.

The data presented in **Figure 4.13** show an increase in the number of nanopores of 0–100 nm with increasing water addition. The 5g water sample had the greatest number of nanopores of 0–100 nm, in agreement with the narrower PSD for this sample in **Figure 4.11**. In addition, the ImageJ data confirm the presence of nanopores for the 1g and 3g samples. In general, the trend observed in **Figure 4.13** is similar to the observation from **Figure 4.11** that an increase in water addition leads to an increase in nanopore formation.

4.4.8 Capillary flow time

CFT data for membranes cast from 4.2% PMMA lacquer at low, medium, and high humidity are presented in **Table 4.8**.

Table 4.8: CFT data obtained for 4.2% PMMA membranes cast at low, medium, and high humidity.

Sample	Capillary flow time (s)			
	A	B	C	Mean
Low humidity	224	228	176	209.3
Medium humidity	447	474	458	459.67
High humidity	996	937	962	965

The data show that the CFT increases with the humidity; this is because the upper limit of evaporation depends on the humidity [12,19]. This humidity-related limit on the evaporation rate will affect the pore sizes formed (**Figure 4.8**) and, as observed for samples described in Chapter 3, the broader the pore distribution, the slower is the capillary flow through a membrane [22].

CFT data for samples cast with added water are presented in **Table 4.9** in comparison to a sample containing no water.

Table 4.9: CFT data obtained for 4.2% PMMA membranes cast with 1, 3, and 5 g of water added to the lacquer.

Sample	Capillary flow time (s)			
	A	B	C	Mean
0 g of water	197	231	223	217
1 g of water	205	201	202	202.67
3 g of water	253	244	262	253
5 g of water	291	297	320	302.67

The CFT increases with the water content, with the exception of the sample with 1 g of added water. The samples with 3 g and 5 g of added water have higher CFTs in comparison to the sample with no water. The sample with no water has a higher CFT than the sample containing 1 g of water. The range of CFT values recorded for triplicate measurements is much narrower for the sample with 1 g of water, which might suggest that this level of water allows the formation of a more uniform pore network. Alternatively, the lack of any significant skinning for this sample may also be a factor in the narrower CFT range.

The samples cast from lacquers containing 3 g and 5 g of water both showed higher CFT than the sample with no added water. This can probably be attributed to the pore distribution, as the pore size distribution is broader for both samples with added water than for the sample with no added water. A broad distribution will limit the maximum speed at which pores can be filled, as the presence of smaller pores limits the flow through to larger pores [22]. This leads to the overall increase in CFT despite the increasing average pore size in the case of water addition of 1 and 3 g.

Statistical analysis results for the differences in CFT in relation to humidity and water addition are shown in **Tables 4.10 and 4.11**.

Table 4.10: Results for t-test pairwise comparisons of capillary flow time in relation to humidity and water addition

Sample comparison	T Value	P Value	Statistically Significant
Low v Medium Hum	13.56515	0.000171	Yes
Low v High Hum	31.61137	<0.00001	Yes
Medium v High Hum	26.8666	0.000011	Yes
0g v 1g	1.3871	0.237599	No
0g v 3g	3.12945	0.03520	Yes
0g v 5g	6.32499	0.003197	Yes
1g v 3g	9.4375	0.000703	Yes
1g v 5g	11.21153	0.00036	Yes
3g v 5g	4.84441	0.008373	Yes

The results in **Table 4.10** show that differences in chamber humidity led to statistically significant changes in CFT, confirming that varying the humidity can influence the CFT time. In the case of samples containing water, the pairwise comparisons revealed statistically significant changes in CFT except for the sample containing no water in comparison to the sample containing 1 g of water (CFT difference not statistically significant). This suggests that the improved CFT of the sample including 1 g of water is not solely due to water inclusion and may also involve the influence of water on reducing skin layer formation.

Similar to the approach described in **Chapter 3** for analysis of differences in CFT in relation to the PMMA concentration, ANOVA within-group testing was also carried out to determine the statistical significance of differences in CFT in relation to humidity and water addition for the two data sets overall. The ANOVA results are presented in **Table 4.11**.

Table 4.11: ANOVA for within-group comparison of capillary flow time in relation to humidity variation and water addition

Data set	F-statistic value	P-value	Statistically Significant
Humidity variation	702.38331	0	Yes
Water addition	37.50452	0.00005	Yes

The results for the two within-group comparisons confirm statistically significant differences in CFT for humidity variation in the chamber during membrane production and for water addition to the membrane casting lacquer.

4.5 Conclusions

The data presented in this chapter demonstrate that, in combination with the PMMA loading, the humidity during casting and the addition of water to the lacquer can be used to refine asymmetric microporous–nanoporous membranes.

Humidity plays a role in pore refinement by decreasing the average pore size and increasing the surface area with as the humidity increases. As described in Chapter 1, the basic principle behind VIPS [23] is that vapour of the non-solvent of choice induces phase separation. However, while water may be considered a non-solvent for PMMA in the acetone–butanol–ethanol system used here, there are significant differences in solvent vapour pressure that will in turn reduce the evaporation rate of the three components. This causes slower phase separation and drying steps, as the solvent and non-solvents in the gel phase will take longer to reach the air interface and finally evaporate. This results in tighter packing of PMMA and gives rise to a broader pore size distribution and the appearance of sub-100 nm structures, as observed for samples cast at medium (23.2–25% RH) and high (45.4–52.5% RH) humidity. These factors in turn cause the lateral flow to slow and affect the CFT time, with an almost fivefold increase in duration; this was verified through ANOVA and t-test statistical analyses, which confirmed that the differences in CFT in relation to humidity variation were statistically significant.

When added to the lacquer, water plays a different role when compared to its presence in the curing medium (air). As noted by Hoogenboom et al. [5], water forms a cage around PMMA molecules, increasing the solubility of the polymer in ethanol and changing the temperature at which phase separation occurs. The transition from “solvent” to non-solvent occurs at a much higher concentration (33 g per 100 ml) than tested in the present study, so it can be assumed that any contributions from water to the system will be as a co-solvent. In relation to pore formation, butanol and ethanol readily form azeotropes [21] with water. Therefore,

inclusion of water in the lacquer gives rise to two further temperatures at which solvents will be removed from the gel matrix as the membranes cure and dry, thus facilitating the role of what may be viewed as additional porogenic material that would not be present in membranes cast without water in the lacquer mix. The changes in morphology play a role in altering the CFT, with an initial drop followed by an increase in CFT duration with increasing water addition. This influence was verified through ANOVA and t-test statistical analyses, which confirmed that the differences in CFT in relation to water addition were statistically significant. The addition of 1 g of water probably improved the lateral flow because of the noticeable decrease in skin layer formation. In summary, a low concentration of water may help in inhibiting skin layer formation and improving membrane functionality.

Water influences the pore morphology of a membrane when included in the lacquer or in the curing medium. From the data gathered, it is evident that humidity played a greater role in changing the pore morphology: higher humidity was associated with a broader pore size distribution and pore sizes in the sub-1- μm range. The solvent suppression effect is most likely to be a greater hindrance to membrane production, with water at low concentrations potentially improving membrane porosity by inhibiting skin layer formation.

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Chapter 5

Modification of PMMA Membranes Through the Use of Additives

Abstract

This chapter describes the effect of adding glycerol and PEG to PMMA membrane lacquers.

Both reagents altered the pore morphology of the membranes produced.

Glycerol addition decreased the pore volume at lower concentrations and increased it at higher concentrations. The average pore size was 1.26 μm for samples with no glycerol addition and 0.99–1.46 μm for samples cast with added glycerol. Skinning was also affected, although the effect was only slight. Samples with no glycerol showed 84.7% coverage, while samples with added glycerol had skin coverage of 74.6–80.6%. The surface area increased from 6.9 $\text{m}^2 \text{g}^{-1}$ for samples with no glycerol to 14.3–15 $\text{m}^2 \text{g}^{-1}$ for samples cast with added glycerol. Lastly, CFT increased from 217 s for samples with no glycerol to 305–471 s for samples cast with glycerol added; the differences in CFT as a function of glycerol addition were statistically significant.

PEG addition altered the membrane pore volume: at lower concentrations PEG increased the pore volume and at higher concentrations it decreased the pore volume. The average pore size decreased from 1.26 μm for samples without PEG to 1.10–1.15 μm for samples with added PEG. Greater PEG addition was also associated with greater nanostructure generation, in particular in the range below 50 nm. Skinning decreased when PEG was added at lower concentrations and returned to values close to those for PEG-free samples on further addition. The skin coverage was 84.7% for samples without PEG and 60.1–83.3% for samples with added PEG. The surface area increased incrementally from 6.9 $\text{m}^2 \text{g}^{-1}$ to 8.8–12.8 $\text{m}^2 \text{g}^{-1}$ with increasing PEG addition. CFT increased from 217 s for samples without PEG to 312–482 s with increasing PEG addition. The differences in CFT as a function of PEG addition were statistically significant.

5.1 Introduction

Modification of PMMA membranes through the addition of other compounds is a route for potentially improving membrane performance in terms of mechanical strength and adhesion to the support. When developing the TIPS–air casting technique, it was observed that PMMA membranes spontaneously delaminated from the Melinex backing film. Some membranes were brittle, leading to fragmentation and breakages when they were being prepared for analysis. In addition, some membranes exhibited uneven solvent fronts during capillary flow tests, which is problematic, as this would indicate either slow restriction due to an inhomogeneous pore size distribution or, in the worst-case scenario, pore collapse and blockage. Therefore, it was decided to investigate whether additives to the PMMA lacquer could improve the integrity and performance of the resulting membranes. To gain further insight into additives with potential to improve PMMA membrane performance, poly(ethylene glycol) (PEG) [126–131] and glycerol [132–136] were chosen as two materials to investigate, as these are commonly used as membrane additives.

In contrast to PMMA, PEG is a hydrophilic polymer and is soluble in water. Other researchers have used PEG to improve the performance of membranes cast from cellulose acetate [128], poly(ether sulfone) [130], and poly(ether imide) [131]. PEG addition to polysulfone membranes increased the pore sizes at higher concentrations and the phase separation tended towards spinodal decomposition at lower concentrations [126]. Other studies conducted with polysulfone showed that PEG can improve the hydrophilicity of membranes [127,129]. It was hypothesised that incorporation of PEG into PMMA lacquers would introduce a secondary porogen that could lead to a secondary pore-size range in the resulting membranes. PEG incorporation can easily be included in the methodology described in Chapter 3, as the washing step should provide sufficient water to remove PEG from the membrane matrix.

Glycerol was chosen as it is a known plasticiser for PMMA [80,137] and has been used for plasticisation of other materials such as chitosan [132], PVDF [98,135], PVA [133] and alginate [136]. Glycerol has also been used as a non-solvent for PVDF [134]. It was hypothesised that incorporation of glycerol should improve membrane integrity and the prevent fractures observed and discussed in Chapters 3 and 4, while also enhancing the water uptake of PMMA membranes and the flow characteristics of the solvent front as liquid flows laterally through the membrane.

5.2 Materials and methods

5.2.1 Materials

PMMA was obtained from Arkema (Altuglas[®] BS572). Acetone (HPLC grade, $\geq 99.5\%$) was purchased from Honeywell. Butanol (HPLC grade, $\geq 99.7\%$) was purchased from Sigma Aldrich and ethanol (HPLC grade, $\geq 99.9\%$) was purchased from Fischer Scientific. Glycerol and PEG (Molecular weight 1000 g mol⁻¹ by GPC) were purchased from Sigma Aldrich. Polyester backing (Melinex 401, 75 μm in thickness) with a slip surface on one side was purchased from Teijin Films. Sodium dodecylbenzene sulfonate (SDBS, technical grade) was purchased from Sigma Aldrich.

5.2.2 PMMA pre-drying

PMMA was dried before lacquer formulation as outlined in Chapter 3.

5.2.3 Lacquer formulation

Solvent blends were formulated using the ratios shown in **Table 5.1**. Solvents were weighed into a 250-mL Duran jar using a Fischer Scientific model PSS6001 analytical balance. After each addition, the balance was set to zero and the lid on the jar was secured. Solvents were added in the order of least to most volatile (butanol, ethanol, acetone). When all three solvents had been added, a magnetic stirring bar (40 mm $\times$ 0.5 mm) was added to the jar, which was then sealed and placed on an IKA RET hotplate held at 40 °C with the magnetic stirrer set to 600 RPM. The solvent mix was stirred for 1 h to ensure homogeneity. Then samples of PMMA previously dried in a Memmert UN55 oven at 60 °C for a minimum of 72 h were added to the solvent mix and the Duran jar was placed back on the hotplate to

allow the PMMA to fully dissolve under stirring for 24 h. To prepare samples containing glycerol or PEG, after the 24-h stirring period the Duran jar was removed from the hotplate and the appropriate mass of glycerol or PEG was added. The jar was then replaced on the hotplate and allowed to stir for a further 24 h.

Table 5.1: Composition of lacquers used for glycerol and PEG addition experiments.

Sample	Lacquer composition (g)					
	PMMA	Acetone	Butanol	Ethanol	Glycerol	PEG
A	4.2	40.6	27.6	27.6	1	—
B	4.2	40.6	27.6	27.6	3	—
C	4.2	40.6	27.6	27.6	5	—
D	4.2	40.6	27.6	27.6	—	1
E	4.2	40.6	27.6	27.6	—	3
F	4.2	40.6	27.6	27.6	—	5

5.3.4 Membrane fabrication

Membranes were fabricated under low-humidity conditions as outlined in Chapter 3 and further detailed in Chapter 4.

5.3 Membrane characterisation

5.3.1 Lacquer characterisation

Lacquers were characterised by measuring the turbidity using a Lovibond TB 100 tintometer during sample cooling, as described in detail in Chapter 3.

5.3.2 SEM imaging

Images of the skin (the open side of the membrane that faces into the air) and belt layers (the closed side of the membrane facing the Melinex) as well as cross-sections of the membrane samples were imaged using a Zeiss Ultra SEM instrument with a Gemini electron optical column and an acceleration voltage of 2.5 keV. Further details are provided in Chapter 3.

5.3.3 Capillary flow time

Samples of the membranes were cut into strips of 4 cm × 1.5 cm across the web from the middle of the cast run and the centre of the membrane, ensuring that the backing remained on the sample. CFT measurements were then carried out and statistical analysis conducted as described in Chapter 3.

5.3.4 BET analysis

BET analysis was performed using a Nova 2400e surface area and pore size analyser (Quantachrome). Before analysis, samples were degassed in an oven at 100 °C for 1 h.

5.3.5 Mercury porosimetry

Mercury porosimetry was performed using an Autoscan-33 porosimeter (Quantachrome) and the pore diameter was then calculated for each membrane sample. Further details are described in Chapter 3.

5.3.6 ImageJ SEM analysis

Analysis of SEM images was performed using ImageJ as described in Chapter 3.

5.4 Results and discussion

5.4.1 Lacquer characterisation

Lacquers were characterised by measuring the turbidity as a function of temperature. The results are presented in **Figures 5.1** and **5.2** and **Tables 5.1** and **5.2**. Data generated from the experiments described in Chapter 3 for the 4.2% PMMA lacquer solution were used for comparison and to determine the effect of additives on the lacquer cloud point.

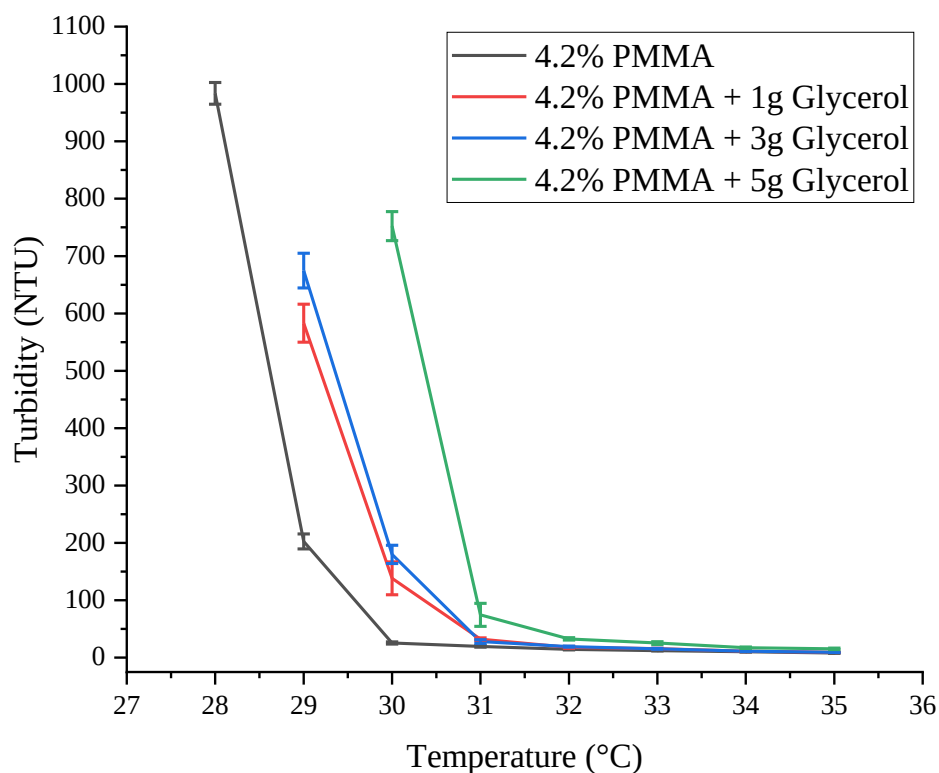


Figure 5.1: Graph of turbidity versus temperature for samples containing 4.2% PMMA and glycerol as an additive.

The results for glycerol addition shown in **Figure 5.1** reveal only a minor change of around 2 °C in cloud point as the glycerol loading is increased. These changes may be due to the slight change in the system χ parameter as glycerol is added. Glycerol acts as a non-solvent for PMMA according to the χ value of 3.97 approximated using the Hansen parameters[138]. When glycerol is incorporated into the lacquer solution, the χ value approximated for the solvent mix using the approach described in Chapter 4 increased from 0.64 to 0.65, 0.68, and 0.71 for addition of 0, 1, 3, and 5 g of glycerol, respectively. While the increase in approximated χ is nominal, it is sufficient to cause a slight increase in turbidity with respect to temperature and consequently an increase in the cloud point temperature. The slight changes in cloud point are as expected, as χ is still less than 1 and thus PMMA will still be soluble in this solvent/non-solvent mixture [90].

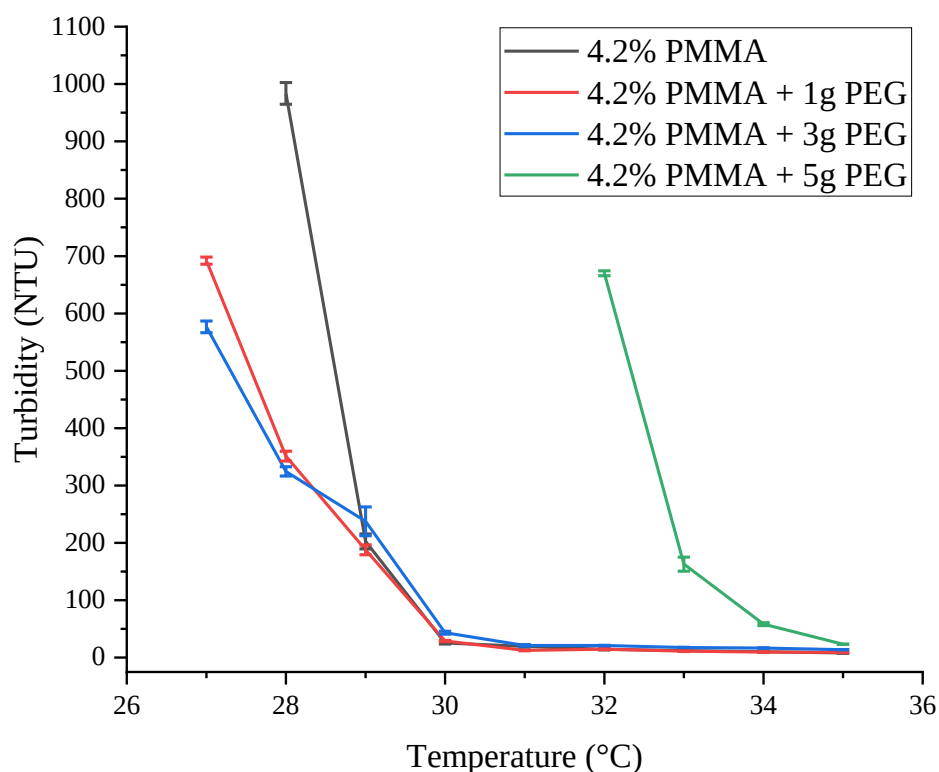


Figure 5.2: Graph of turbidity versus temperature for samples containing 4.2% PMMA and PEG as an additive.

The results for PEG addition shown in **Figure 5.2** reveal a slight decrease in cloud point for addition of 1 and 3 g and a significant increase in cloud point for addition of 5 g of PEG. In this case there are two solvent–polymer interactions that need to be considered: the solvent–PMMA interaction and the solvent–PEG interaction, both of which may contribute to the turbidity of the solution. Using the Hansen solubility parameters, χ approximations for PEG and PMMA were calculated as 0.05 and 0.64, respectively [138], suggesting that PEG is more soluble than PMMA in this solvent mix. This is as expected, as PEG is soluble in both acetone and alcohols [139]. As both polymers are soluble in the solvent–non-solvent blend, the variations in cloud point may be due to PEG–PMMA interactions. Only a slight effect was observed for 1 and 3 g of PEG, while the effect was more pronounced in the case of 5

g, suggesting that if the hypothesis of a PEG–PMMA interaction is correct, it may depend on the PEG loading in the lacquer. In the case of the 5 g PEG sample, the mass of PEG is greater than the mass of PMMA included in the lacquer, so this higher loading may be the cause of the increase in cloud point.

5.4.2 Membrane appearance

Membranes cast with glycerol were generally matte white but some regions had a glossy appearance, which was more prevalent for the 3 g and 1 g samples. All samples adhered to the backing and no delamination was observed, with membranes only removable via scraping with a scalpel. When removed from the backing, the membranes were more robust than samples cast with no glycerol. Greater force was required to break the membranes and they cracked along the bend point as opposed to the fracturing or shattering observed for samples without an additive, as discussed in Chapters 3 and 4.

The matte appearance of the membranes was as expected, as this was the case for all previous samples. The presence of glossy regions suggests that there were some pristine skinned regions, as a similar effect with pristine skin layers was observed for samples cast at higher PMMA concentrations, as discussed in Chapter 3.

Membrane adhesion to the Melinex backing is most likely due to an interaction between the slip surface and glycerol. As noted previously, the nature of the slip surface is unknown and as such any conclusions are only speculative.

The improved mechanical properties were as expected, as membrane plasticisation generally leads to better mechanical strength [80,81]. This is because plasticiser addition decreases the glass transition temperature of a polymer, resulting in increased free movement of polymer chains [113], which in turn allows more flexibility in the resulting membrane.

Samples cast with PEG were matte white in appearance with no visual differences noted between additions of 1, 3 or 5 g of PEG. Membranes exhibited good adherence to the Melinex backing, with no signs of delamination. For removal, the backing was folded, after which it was easy to detach the membrane from the Melinex. When removed from the backing, membranes were less brittle than the PMMA membranes without additives

discussed in Chapters 3 and 4, and showed better mechanical properties in the order $1\text{ g} < 3\text{ g} < 5\text{ g}$ of PEG.

The matte white appearance of the membranes was as expected, as this was the case for the PMMA membranes discussed in Chapters 3 and 4.

The improved adherence, similar to the case for glycerol as an additive, is only speculative; however, it can generally be stated that PEG altered the interaction between PMMA and the slip surface on the Melinex backing.

An interesting finding was that PEG improved the mechanical properties of the PMMA membranes; a similar effect was observed for PEG 1500 when used as an additive for polysulfone membranes [127]. In this case, some degree of plasticisation may have occurred, as an increase in mechanical strength is a characteristic of plasticised membranes [80,81].

5.4.3 SEM imaging

Figure 5.3 shows SEM images of membrane samples cast with 1, 3, and 5 g of glycerol added to stock 100-g samples of 4.2% PMMA lacquer solution.

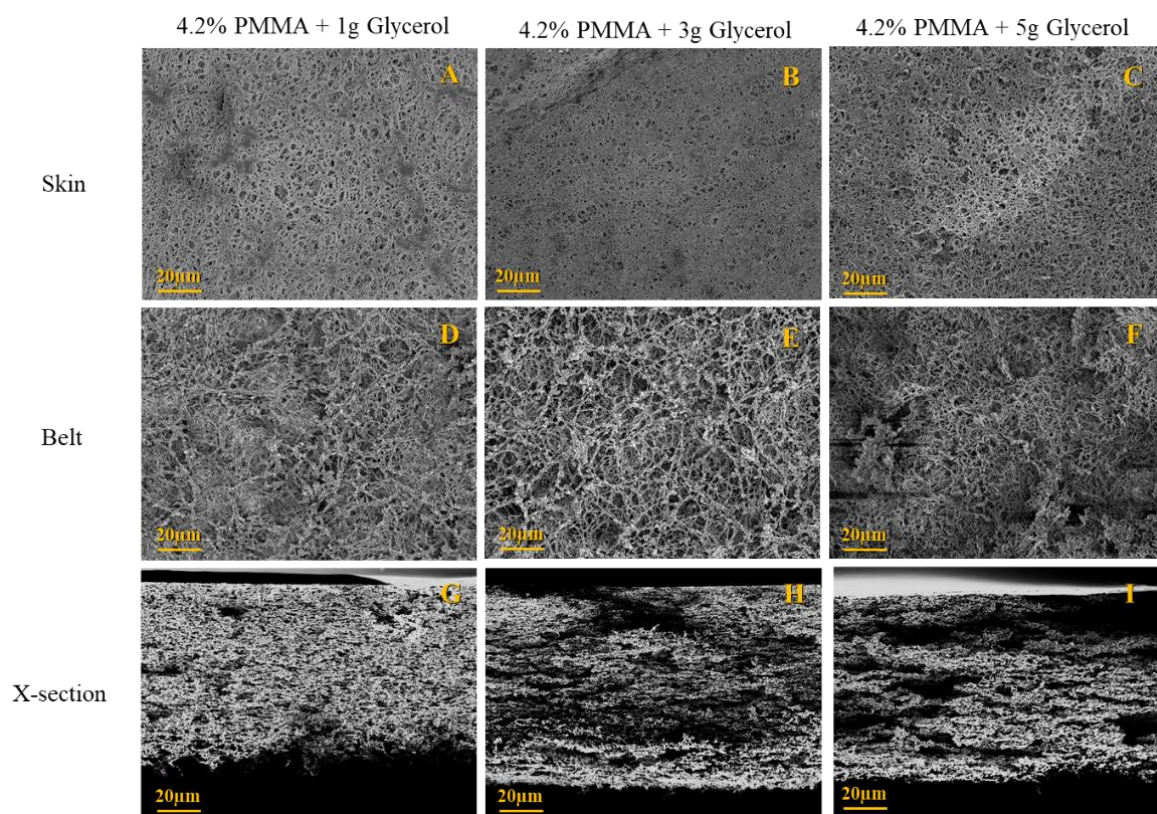


Figure 5.3: SEM images of skin and belt layers and cross-sections of membranes cast from 4.2% PMMA with 1, 3, and 5 g of added glycerol.

SEM images of the skin layer for samples with added glycerol all show some degree of skinning, with the degree of skinning increasing in the order $5\text{ g} < 1\text{ g} < 3\text{ g}$ of glycerol. There appears to be no simple trend for skin layer formation in relation to the glycerol addition. Any changes in structure may be a result of increased plasticisation of the PMMA chains as well as the change in cloud point observed, which would result in a higher concentration of PMMA at the air interface as the membrane forms. Glycerol may also be acting as a non-solvent in this instance. This phenomenon has been observed for PVDF [134]

and glycerol may contribute to swelling of the polymer, as ethanol and butanol do [105]. At lower concentrations glycerol may have a greater influence as a non-solvent, as samples with 1 g and 3 g of glycerol had denser or more pristine skin layers, in contrast to the 5 g sample, which exhibited less pristine skinning. This may be attributed to increased plasticisation in the bulk, whereby glycerol molecules are more likely to have interacted with the polymer at higher concentrations, increasing swelling and remaining in the gel network throughout the curing process.

The belt layer showed an increasingly more open structure as more glycerol was added. This is due to the plasticisation effect, whereby glycerol molecules are deposited between polymer chains, which in turn increases the free volume of samples in comparison to samples without plasticiser [80,81].

The cross-sectional images of the bulk porosity reveal that membranes cast with 3 g and 5 g of glycerol appear to be more porous than the sample cast with 1 g of glycerol. This can probably be attributed to the free volume factor previously mentioned, which is a known effect of plasticisers: an increase in plasticiser concentration leads to an increase in free volume [80].

Figure 5.4 shows SEM images of membranes cast from samples with 1, 3, and 5 g of PEG added to stock 100-g samples of 4.2% PMMA lacquer solution.

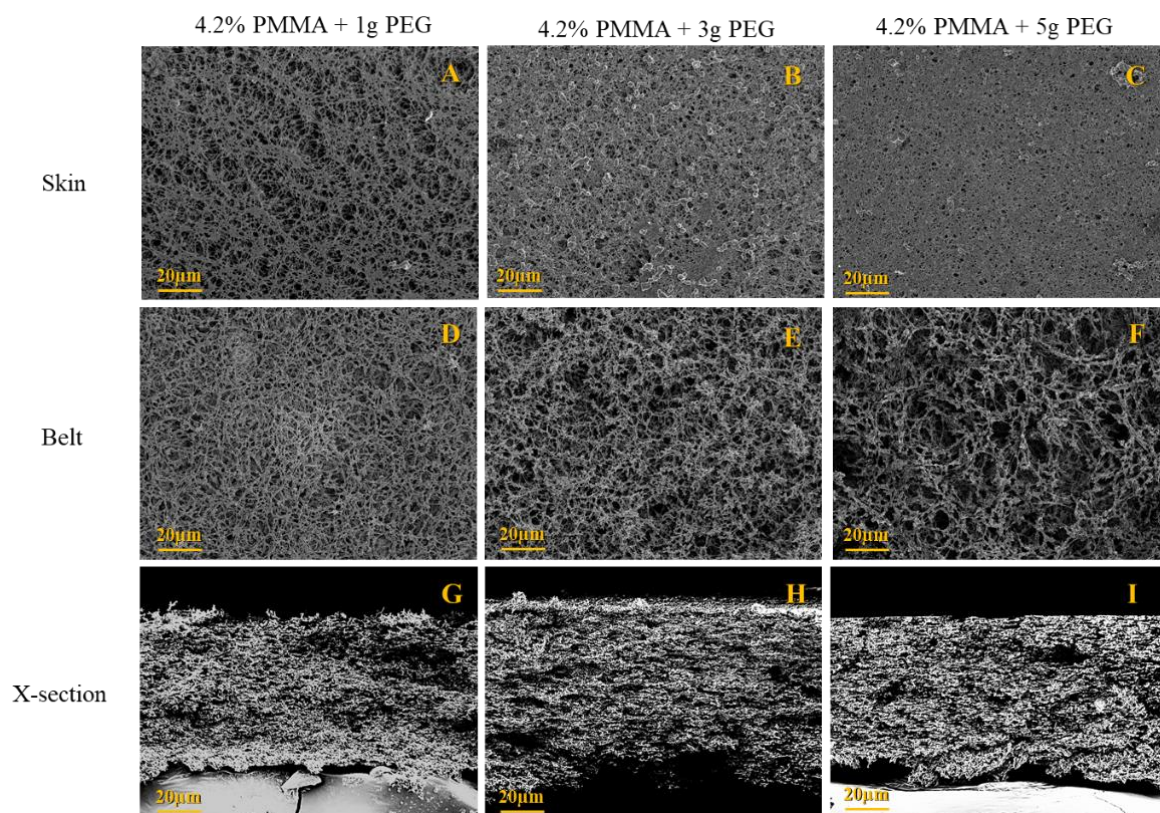


Figure 5.4: SEM images of skin and belt layers and cross-sections of membranes cast from 4.2% PMMA with 1, 3, and 5 g of added PEG.

The images show an increase in skinning with increasing PEG addition. The open porous structure observed for the 1 g sample may be due to accumulation of PEG at the air interface that subsequently melts as the air temperature is increased to 60 °C, as the melting point of PEG is 54–58 °C [139]. Any residual PEG that is left on the skin layer is then removed when samples are washed in water. In comparison, increased skinning is observed for the 3 g sample, along with a significant number of agglomerates formed on the skin layer. Similar agglomerates were previously seen for other samples, but not to the same extent. This suggests that the agglomerates are PMMA and in this case that PEG plays some role in the increased formation of these agglomerates. In contrast to the 1 g and 3 g samples, addition of 5 g of PEG seems to have drastically increased the skinning. The cloud point for this lacquer was 33 °C (**Figure 5.2**), which would lead to more rapid nucleation and faster

migration of the polymer towards the air interface during curing, in turn increasing the local concentration of PMMA and leading to near total skinning [76]. In addition, there are two regions where agglomeration occurred and it is likely that PEG played some role in their formation.

Images for the belt layer show an increasingly open structure as the PEG loading was increased. This trend is as expected, as there are three possible mechanisms for PEG removal from the membranes: (1) via melting when the curing temperature for membranes reaches 60 °C; (2) via dissolution in water when the membranes are washed after curing; and (3) via melting of any residual PEG traces when the membranes are dried for 24 h in an oven. These three mechanisms do not affect the PMMA but result in a more open structure in the belt layer as PEG is removed from the membrane.

The cross-sectional images reveal that the membranes possess bulk porosity and, similar to the membranes described in Chapters 3 and 4, are asymmetric, with a less porous skin layer, a more open belt layer, and overall bulk porosity.

5.4.4 Mercury porosimetry

Figure 5.5 shows porograms for membranes cast with 1, 3, and 5 g of added glycerol in comparison to a sample containing no glycerol.

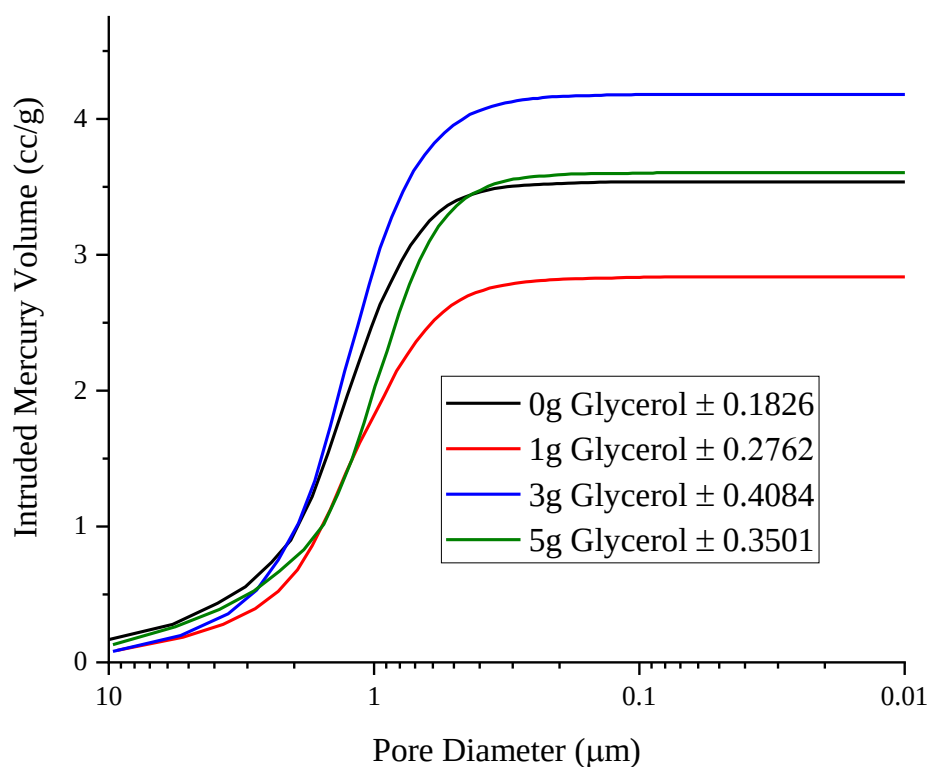


Figure 5.5: Porograms for 4.2% PMMA membrane samples cast with 0, 1, 3, and 5 g of added glycerol.

The results show that the pore volume decreased when 1 g of glycerol was added and increased when 3 g and 5 g glycerol were added in comparison to a membrane with no glycerol. The greatest increase in pore volume was observed for the sample with 3 g of glycerol. The results suggest that there may be a threshold for the glycerol concentration above which an increase in free volume occurs. In addition, the decrease in pore volume for 5 g compared to 3 g of glycerol suggests that there may also be an upper threshold for the effect of glycerol on increasing the pore volume.

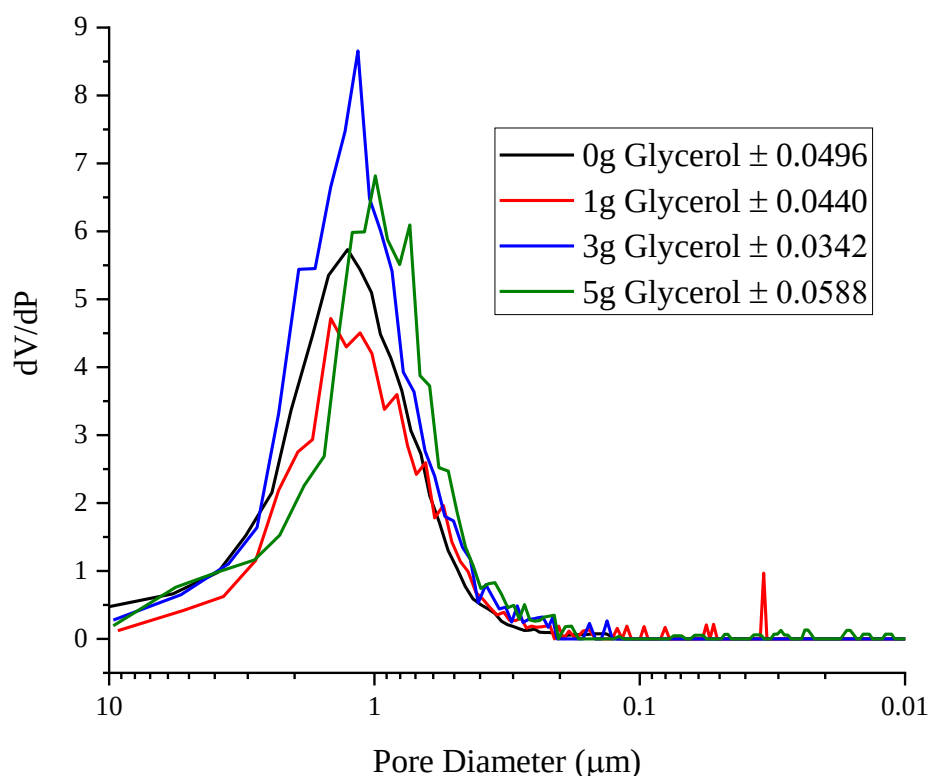


Figure 5.6: Pore size distribution for 4.2% PMMA membrane samples cast with 0, 1, 3, and 5 g of added glycerol.

Results for the pore size distribution in **Figure 5.6** show that addition of glycerol led to an increase in the formation of nanostructures in all samples. The average pore size was 1.26, 1.46, 1.15, and 0.99 μm for glycerol addition of 0, 1, 3, and 5 g, respectively. Furthermore, additions of 3 g and 5 g appeared to eliminate the sub-100 nm structures observed for the 0 g and 1 g samples. This may be a result of a change in PMMA properties under the influence of glycerol. In addition, the increase in cloud point observed (**Figure 5.1**) will allow for a quicker phase separation when the lacquer is deposited, which in turn may result in fewer nanostructures because of more rapid migration of the solvents to the air interface and faster PMMA gelation.

Figure 5.7 shows porograms for membranes cast with 1, 3, and 5 g of added PEG in comparison to a sample containing no PEG.

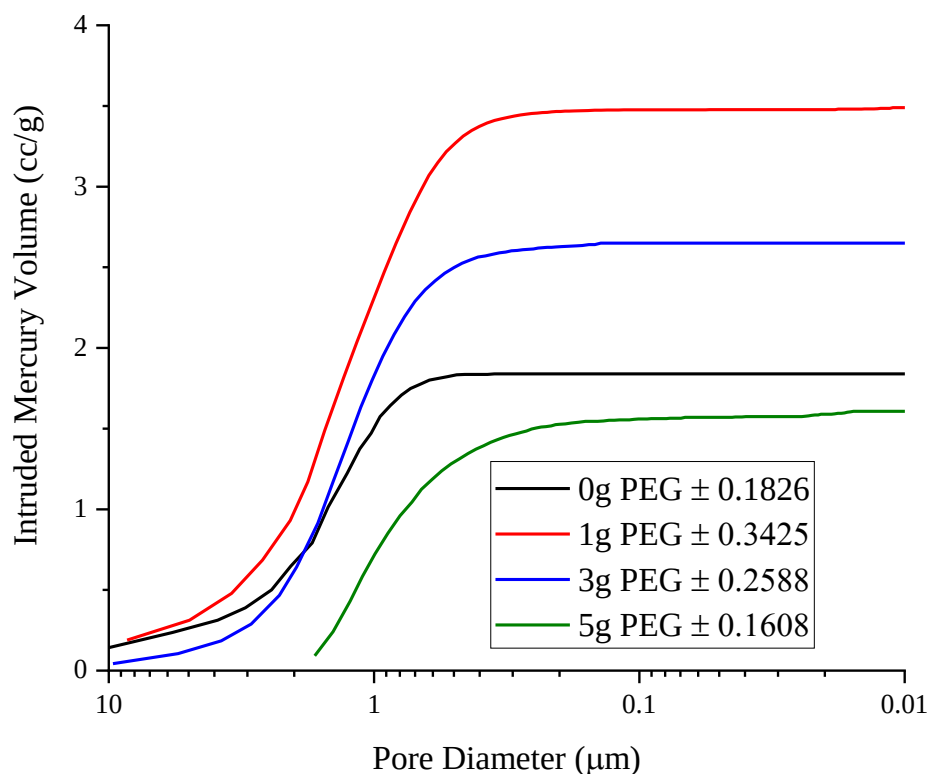


Figure 5.7: Porograms for 4.2% PMMA membrane samples cast with 0, 1, 3, and 5 g of added PEG.

The decrease in pore volume observed with increasing PEG loading is most likely due to the packing of PMMA before PEG removal via melting and washing with water. A linear decrease in pore volume was observed when the PEG content was increased from 1 g to 3 g to 5 g (3.53, 2.68, and 1.97 cm³ g⁻¹, respectively). This suggests that the decrease in pore volume may be attributable to changes in the PMMA packing under the influence of PEG during the phase separation process.

Figure 5.8 shows the pore size distribution for membranes cast with 1, 3, and 5 g of added PEG in comparison to a sample with no PEG.

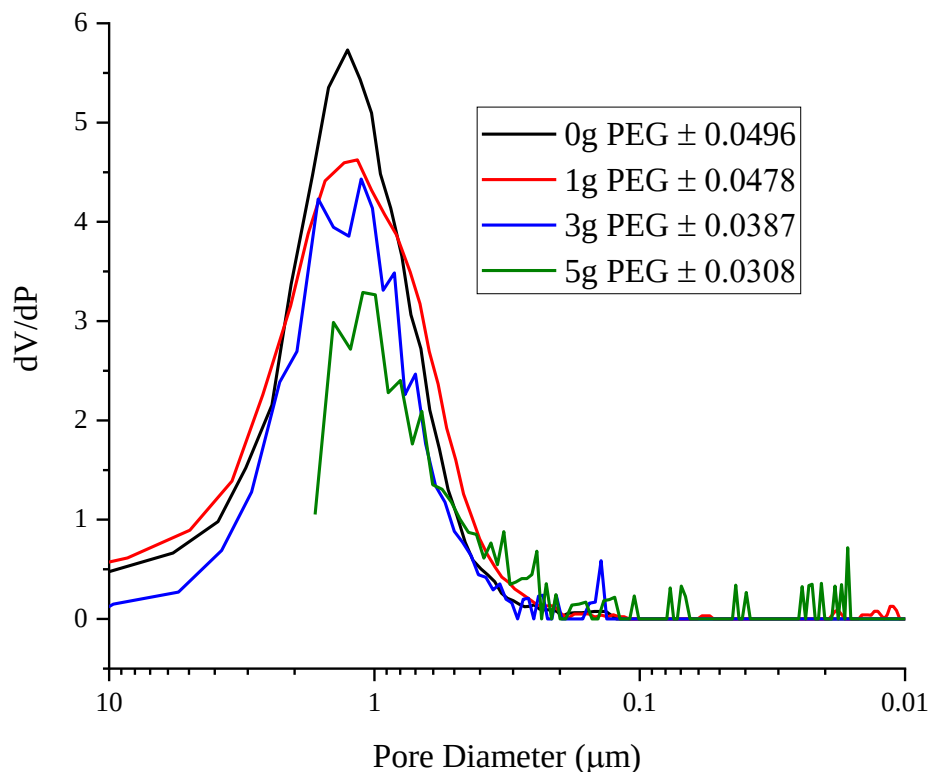


Figure 5.8: Pore size distribution for 4.2% PMMA membrane samples cast with 0, 1, 3, and 5 g of added PEG.

Figure 5.8 shows that as the PEG loading was increased, a greater number of nanopores were generated, while the morphology of the bulk membrane remained in the microporous region. The average pore size was 1.26, 1.15, 1.12, and 1.10 μm for PEG addition of 0, 1, 3, and 5 g, respectively. This is most likely a result of agglomeration of PEG within the bulk membrane and the molecular size of each PEG polymer strand. In the case of the 5 g sample, a greater proportion of pores were generated in the 11 nm range. This may be because of the higher cloud point for this lacquer (**Figure 5.2**): a higher cloud-point temperature may lead to faster phase separation and gelation of the PMMA and PEG, which in turn may have resulted in deposition of PEG as a lone polymer throughout the membrane. This peak is only

present in the 5 g sample; while there are nanostructures below 11 nm for the 1 g sample, it is more likely that these structures formed independent of PEG, as they are present in the sample without PEG. Furthermore, the 5 g sample has no visible pores $>2\ \mu\text{m}$. However, this is likely because the larger pores are $>7\ \mu\text{m}$, as the resolution of the instrument is $7\ \mu\text{m}$. Any pores larger than $7\ \mu\text{m}$ are likely to be filled during the initial stages of sample loading and before the sample is put under pressure. This assumption is based on the SEM images of the belt layer presented in **Figure 5.4** in which there appear to be some pores of $\sim 10\ \mu\text{m}$ that were not seen in any previous samples prepared. This may give a false reading for the total pore volume and pore distribution, which may in fact be higher than the recorded values that are presented in **Figure 5.7** and **Figure 5.8**.

5.4.5 BET data

BET data for samples cast from lacquers with added glycerol are shown in **Table 5.2** in comparison to a sample with no added glycerol.

Table 5.2: Surface area data generated from BET analysis for membranes cast from 4.2% PMMA with 1, 3, and 5 g of glycerol added to the lacquer.

Sample	Surface area ($\text{m}^2\ \text{g}^{-1}$)
4.2% PMMA	6.9 ± 0.08
4.2% PMMA +1 g glycerol	14.7 ± 0.49
4.2% PMMA + 3 g glycerol	15 ± 0.37
4.2% PMMA +5 g glycerol	14.3 ± 0.33

It is evident that the surface area increased on addition of glycerol, probably because of a combination of the increase in volume associated with plasticiser addition [80] and an increase in nanopore formation. As mentioned previously, there may be lower and upper limits for the glycerol concentration associated with achieving maximum surface area and

pore volume; the optimum concentration is probably between 3 g and 5 g of glycerol, as the surface area was higher for the 3 g glycerol sample than for both the 1 g and 5 g samples.

BET data for samples cast from lacquers with added PEG are shown in **Table 5.3** in comparison to a sample with no added PEG.

Table 5.3: Surface area data generated from BET analysis for membranes cast from 4.2% PMMA with 1, 3, and 5 g of PEG added to the lacquer.

Sample	Surface area ($\text{m}^2 \text{g}^{-1}$)
4.2% PMMA	6.9 ± 0.08
4.2% PMMA +1 g PEG	8.8 ± 0.21
4.2% PMMA + 3 g PEG	11 ± 0.29
4.2% PMMA +5 g PEG	12.8 ± 0.37

The increase in surface area with increasing PEG loading is as expected, as there was an increase in nanopore structures observed in the pore size distributions presented in **Figure 5.8**.

5.4.6 ImageJ SEM analysis

Results for the percentage skin layer coverage are presented in **Table 5.4** for samples with and without added glycerol and in **Table 5.5** for samples with and without added PEG.

Histograms of pore sizes detected in these samples are presented in **Figure 5.9** and **Figure 5.10**, respectively. The SEM images presented in **Figures 5.3** and **5.4** were used for ImageJ analysis. As described in **Section 3.3.7**, the images were sharpened prior to analysis to allow easier detection of skin boundaries and defects in the skin layer when processing the images and give greater accuracy in measuring skin coverage.

Table 5.4: Percentage skin coverage for PMMA membrane samples cast with addition of 1, 3, and 5 g of glycerol.

Sample	Skin layer coverage (%)
0g glycerol	84.71
1g glycerol	77.26
3g glycerol	80.60
5g glycerol	74.63

The data presented in **Table 5.4** show that skin coverage decreased on addition of glycerol, in line with visual observations for the SEM images presented in **Figure 5.3**. No definitive trend is apparent for skin layer coverage as a function of increasing addition of glycerol to the lacquer, with coverage remaining fairly similar for the 1g, 3g, and 5g samples (variation of 2.44%, standard deviation). There is an increase from 1g to 3g, followed by a decrease from 3g to 5g, which may indicate that the magnitude of glycerol addition has little effect on skinning. This result is not unexpected, as the primary role of glycerol when added to the lacquer is as a plasticiser to increase polymer chain mobility as opposed to an agent to alter the overall membrane make-up or the phase separation mechanism [9,10].

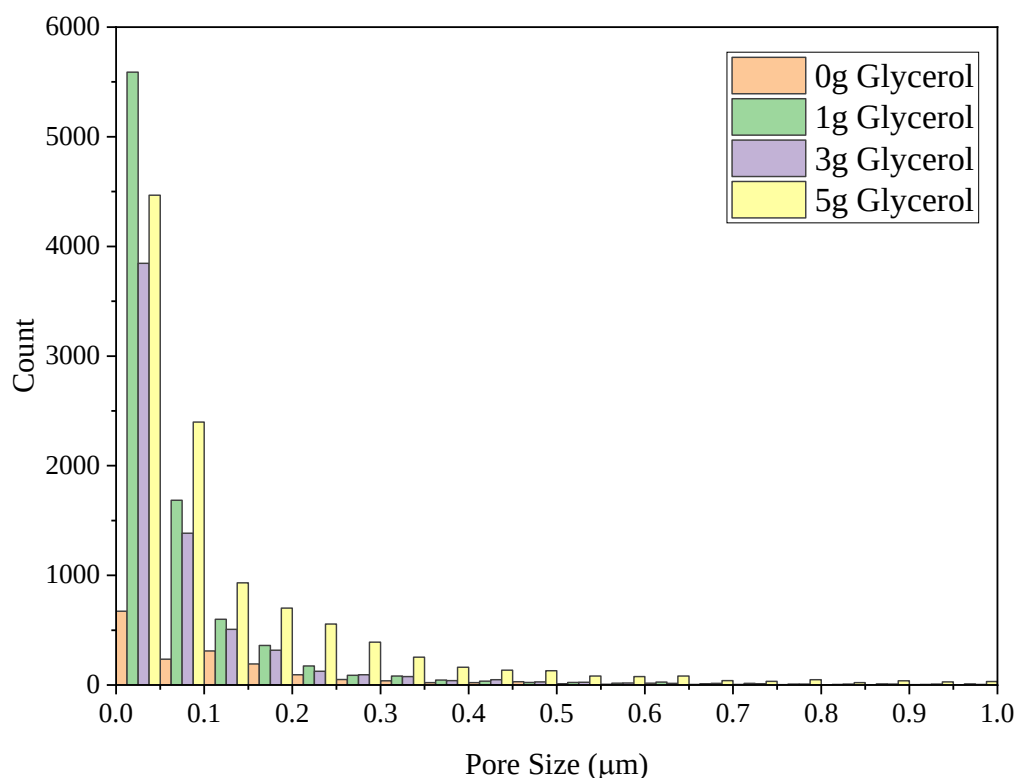


Figure 5.9: Histogram of pore sizes detected using ImageJ for membranes cast with 0, 1, 3, and 5 g of added glycerol.

The data presented in **Figure 5.9** show no obvious trend for pore size variation as a function of glycerol addition. The greatest count for pores <50 nm was observed for 1 g of glycerol, whereas the greatest counts for pore sizes in the range 100–900 nm were observed for 5 g of added glycerol. For pore sizes >250 nm, there appears to be a trend whereby an increase in glycerol addition led to a greater pore count per size category. This trend seems to be in line with the PSD trend observed in **Figure 5.6**. The large proportion of pores of 0–50 nm in size for the 1g sample in **Figure 5.9** corresponds to the peak observed at 30–40 nm in **Figure 5.6**, while both the PSD in **Figure 5.6** and histogram in **Figure 5.9** confirm that nanopore formation occurred in the 3g and 5g samples.

Table 5.5: Percentage skin coverage for PMMA membrane samples cast with 0, 1, 3, and 5 g of PEG added to the lacquer.

Sample	Skin layer coverage (%)
0g PEG	84.71
1g PEG	60.97
3g PEG	78.70
5g PEG	83.25

The data in **Table 5.5** show that PEG addition at 1 g led to a decrease in skin coverage from 84.71% to 60.97%. Further PEG addition led to increases to 78.70% at 3 g and 83.25% at 5 g. The lower skin coverage for addition of 1 g of PEG may be related to PEG occupation of regions of the skin layer during curing. These PEG molecules in the skin layer are then removed during the washing step as PEG is soluble in water, leading to lower skin coverage in comparison to the membrane without PEG. This effect diminished at the higher PEG concentrations, especially for 5 g of PEG. In this case the cloud point and the phase separation occur at a higher temperature, resulting in more rapid phase separation which in turn may prevent the PEG from settling in the skin layer and leading to reduced skinning. Thus, the percentage coverage for this sample is only very slightly lower than for the membrane without PEG.

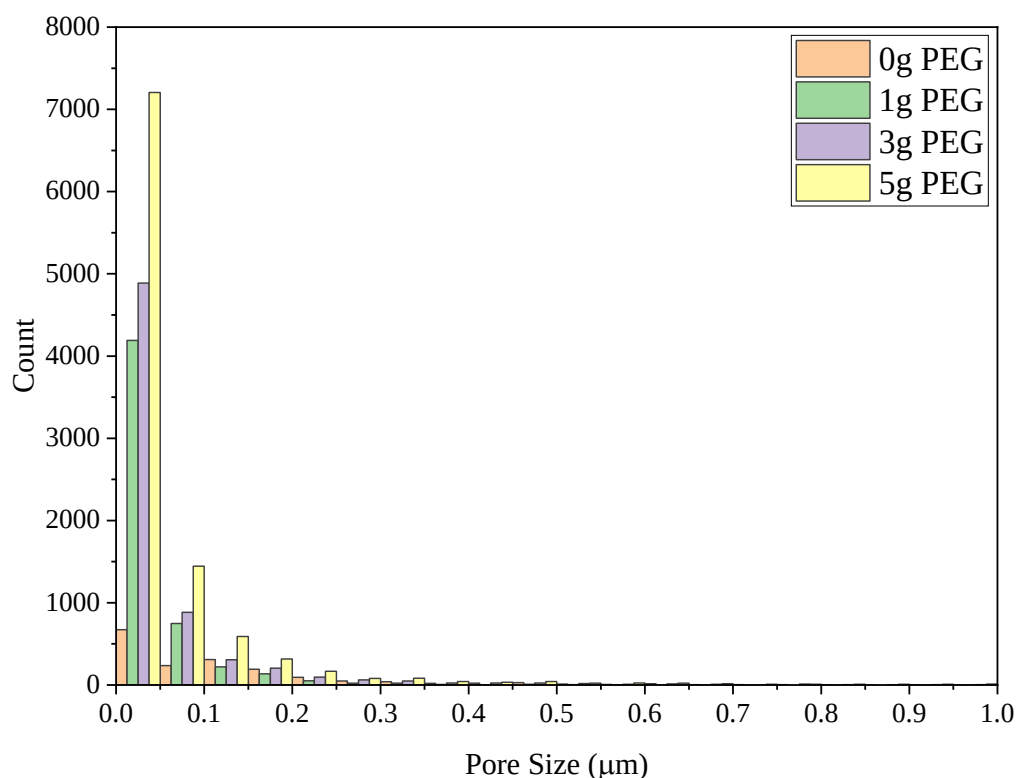


Figure 5.10: Histogram of pore sizes detected using ImageJ for 2.5–10g PMMA membranes with and without PEG addition.

The data presented in **Figure 5.10** show increasing nanopore formation as the PEG concentration is increased, in agreement with the PSD data shown in **Figure 5.8**. Most prominently, addition of 5 g of PEG led to the formation of a large number nanopores of <50 nm in size, in concordance with the nanopores of <30 nm observed in **Figure 5.8**. Thus, the data presented in **Figures 5.10** and **5.8** show similar trends. This can be attributed to removal of PEG embedded in the PMMA web during the washing step, as PEG is water soluble. The pore size is probably dictated by the much lower M_n for PEG (1000 g mol^{-1}) in comparison to the PMMA used ($440,500 \text{ g mol}^{-1}$).

5.4.7 Capillary flow time

CFT data for samples cast with 1, 3, and 5 g of added glycerol in comparison to a sample containing no glycerol are presented in **Table 5.4**.

Table 5.4: CFT data obtained for 4.2% PMMA membranes cast with 1, 3, and 5 g of glycerol added to the lacquer.

Sample	Capillary flow time (s)			
	A	B	C	Mean
0 g of glycerol	197	231	223	217
1 g of glycerol	469	481	463	471
3 g of glycerol	340	378	368	362
5 g of glycerol	270	305	341	305.3

The data in **Table 5.4** show that the CFT first increased when 1 g of glycerol was added and then decreased as the glycerol addition was increased to 3 g and 5 g for a 4.2% PMMA lacquer. The initial drop in CFT can be attributed to the development of nanostructures not present in the 4.2% PMMA sample. Higher concentrations of glycerol (3 g and 5 g) in the lacquer may have had a greater surfactant effect, reflected in an increase in water uptake by the membranes and a decrease in CFT compared to the 1 g sample. Furthermore, the lack of any nanostructures <100 nm for the 3 g and 5 g samples may also contribute to the lower CFT. Nanostructures <100 nm were observed for membranes produced from the samples with 0 g and 1 g of added glycerol, and their absence at higher glycerol loads suggests that CFT will be faster in comparison to the 1 g sample because a lower pore size affects the flow speed [106].

CFT data for samples cast with added PEG are presented in **Table 5.5** in comparison to a sample containing no PEG.

Table 5.5: CFT data obtained for 4.2% PMMA membranes cast with 1, 3, and 5 g of PEG added to the lacquer.

Sample	Capillary flow time (s)			
	A	B	C	Mean
0 g of PEG	197	231	223	217
1 g of PEG	317	312	307	312
3 g of PEG	373	401	409	394.3
5 g of PEG	482	492	474	482.66

The data in **Table 5.5** show that the CFT increased with the PEG concentration. This can be attributed to the increase in the proportion of nanostructures observed in samples containing 1, 3, and 5 g of PEG. As hypothesised for previous samples, nanostructures limit the uptake of water and will be the limiting factor for the CFT [106] .

Statistical analysis results for the differences in CFT in relation to glycerol and PEG addition are shown in **Tables 5.6 and 5.7**.

Table 5.6: Results for t-test pairwise comparisons of capillary flow time in relation to glycerol and PEG addition

Sample comparison	T Value	P Value	Statistically Significant
Glycerol			
0g v 1g	21.99705	0.000025	Yes
0g v 3g	9.465479	0.000695	Yes
0g v 5g	3.85355	0.018247	Yes
1g v 3g	8.68993	0.000965	Yes
1g v 5g	7.82604	0.001439	Yes
3g v 5g	2.4175	0.07296	No
PEG			
0g v 1g	8.9106	0.000877	Yes
0g v 3g	11.83685	0.000292	Yes
0g v 5g	23.08449	0.000021	Yes
1g v 3g	7.29315	0.001879	Yes
1g v 5g	28.6665	0.00001	Yes
3g v 5g	7.30496	0.001868	Yes

The results in **Table 5.6** show that for glycerol addition the difference in CFT was statistically significant for all pairwise comparisons except for 3 g vs 5 g. This indicates that the difference in CFT between samples with 3 g and 5 g of glycerol in the lacquer was not due to the increase in glycerol concentration alone. In the case of PEG addition, all pairwise comparisons revealed a statistically significant difference in CFT.

To supplement the pairwise t-test comparisons, ANOVA within-group testing was also carried out to determine the statistical significance of differences in CFT for the two data sets overall. The ANOVA results are presented in **Table 5.7**.

Table 5.7: ANOVA for within-group comparison of capillary flow time in relation to glycerol and PEG addition

Data set	F-statistic value	P-value	Statistically Significant
Glycerol	66.33743	0.00001	Yes
PEG	198.49408	0	Yes

The results for the two within-group comparisons confirm statistically significant differences in CFT for both data sets, indicating that the inclusion of either glycerol or PEG in the lacquer led to the change in CFT recorded for the membrane samples.

5.5 Conclusions

The data presented indicate that both glycerol and PEG can be utilised to change the PMMA membrane morphology. Both will affect the pore size distribution, resulting in an increase in the formation of nanopores. This effect was more pronounced for the PEG/PMMA samples. While both additives changed the PMMA membrane morphology, PEG seems to act like a sacrificial porogen and appears to be removed entirely following membrane formation via melting and subsequent dissolution in water. By contrast, glycerol acts as a plasticiser, changing the properties of PMMA and consequently the structure of the resulting membrane.

It is difficult to determine whether inclusion of PEG in the lacquer and subsequent membranes had a surfactant effect. The low melting point of PEG and its solubility in water may lead to total removal of PEG before CFT measurement. Therefore, no definite conclusions can be drawn regarding whether PEG improves the membrane wettability. However, the data gathered suggest that any influence it might have on wettability is negligible at best. The data indicate that glycerol influenced the wettability to some degree; however, the exact extent is difficult to determine as there was a decrease in sub-100-nm structures associated with increased glycerol loading. Therefore, further studies are needed to quantify the extent of the improvement in membrane wettability.

For both glycerol and PEG, addition to the lacquer led to statistically significant differences in CFT for the resulting membranes.

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Chapter 6

Final Conclusions and Future Work

6.1 Final conclusions

The work described in this thesis quantitatively demonstrated that it is possible to use a TIPS–air casting process to produce PMMA membranes in a robust, repeatable and scalable manner.

For use in lateral flow assay, large pore sizes are required to carry both biological molecules and nanoparticles used as indicators. Flow times are thus high and a critical element of functionality. The results presented in Chapter 3 indicate that for the fastest CFT time, PMMA loading should be kept below 5 g per 100 ml of solvent. This loading helps to mitigate the formation of dense skin-layer regions; however, skin layers still represent an issue that requires further work to address. We suggest that these membranes should be carried forward and tested for use in general immunoassay devices; the pore morphology would best suit filtration of bacteria and could have potential use for filtering colloids and emulsions [5]. While higher PMMA loadings led to denser skin layers, they also provided narrower pore distributions, which could prove useful in the filtration field, particularly for ultrafiltration, for which pore sizes of 10–100 nm may be required [5].

Chapter 4 presented the effects of water as an added solvent and humidity on membrane morphology. As the humidity was increased, a reduction in pore size was observed. While this result is inconvenient when looking for a rapid CFT, this process control of the humidity could be utilised to produce PMMA membranes with microporous and nanoporous structures as desired. These may have critical applications in separation. Water as an added solvent appears to improve CFT at low concentrations (~1 wt/wt%), while a further increase in the water concentration above in the casting lacquer increases the CFT. While this seems promising, there is a trade-off, as addition of water was associated with a detrimental effect on the mechanical strength of the resulting membranes. Furthermore, water addition can be used to manipulate the pore size of membranes; however, it broadens the pore distribution in the 1 μm range, in contrast to humidity, which induced new nanostructures smaller than

100 nm. Water should be considered as an additive at low concentrations, but addition of an appropriate plasticiser to overcome the detrimental effect on the mechanical properties of the resulting membranes needs to be explored further.

Chapter 5 examined the addition of glycerol and PEG in attempts to overcome slower CFT and membrane brittleness. This is a practical problem because membranes can require pressure to be applied across them. Glycerol addition improved the mechanical properties and the membranes obtained were more robust during handling. Glycerol also seemed to affect the pore size of membranes, with some nanostructures observed in all membranes cast from lacquers containing glycerol. In terms of CFT, glycerol addition first drastically increased the CFT, followed by a decrease as the glycerol loading was increased. PEG, in contrast to glycerol, acted as a sacrificial porogen and led to an increase in nanostructures produced in the membranes as the PEG loading in the casting lacquer was increased. This led to increases in CFT as the PEG loading was increased. It was also noted that PEG, at least in part, improved the mechanical properties of the PMMA membranes, possibly through plasticisation.

In general, the membranes produced during the work carried out for this thesis set a baseline for future work and represent a starting point for PMMA membranes as an alternative to NC. However, there is still a considerable amount of work that could be done to improve the PMMA membranes and make them more viable as an industry standard. Furthermore, from an academic perspective, there is a vast amount of research that could be explored to expand the field of aircast PMMA membranes.

6.2 Future work

From the data gathered and the methodologies developed for the work presented here, the logical next steps would be to test the protein binding capacity of the membranes described throughout this thesis. If initial trials failed to produce adequate protein binding, studies on PMMA functionalisation using oxygen plasma to improve protein binding to the PMMA surface should be carried out, as demonstrated by Kang et al. [1].

Should protein striping trials prove successful, the viability of scale-up of the process discussed in Chapter 3 should be pursued. While costly, such trials could identify whether the process developed is transferable to an industrial setting. However, it should be noted that when going from a pilot study to industrial scale-up, a number of issues may arise, as the design of an industrial air casting machine could be significantly different from the laboratory setup outlined in Chapter 2. Any scale-up would require a number of runs to attempt to reproduce the membranes produced on the pilot rig. Some difficulties may arise, as most industrial scale air casting rigs operate as a continuous process, while all work undertaken for this thesis utilised a batch process. Therefore, any industrial-scale machine would need to be closely monitored so that variations in parameters such as the air flow rate and specifically the humidity are kept to an absolute minimum. While challenging, this task should not be impossible with properly designed equipment.

From a process point of view, there are a number of areas that could be improved upon. Suitable air casting equipment could give finer control over parameters such as the air flow rate, air temperatures, and humidity levels, and an attenuated motor would facilitate operation as a continuous process; these issues were highlighted in Chapter 2 and are predominantly budget-related constraints. If these upgrades could be achieved, an interesting study would be to further investigate the effect of humidity on the pore size distribution by running a series of experiments in which the RH is increased from 0% to 100% in 10% increments; an incremental increase in nanopore formation would be a useful result. While

the results presented in Chapter 4 show that an increase in RH leads to an increase in nanopore formation, there is limited control over the exact RH that can be achieved. Installation of a more robust system should allow more precise control of the RH. Such research would have merit in both academic and industrial terms, with further studies potentially leading to increased knowledge on how to target a specific pore distribution through manipulation of the humidity during membrane production.

One critical, further area that should be improved on or eliminated is the production of skin layers on membranes. Skin layers represent possibly one of the greatest obstacles to producing more rapid membranes. One of the quickest ways to reduce skin layers is to decrease the curing time by increasing the evaporation rates of the solvent and non-solvents. In order to achieve this, a new bed array may be required, as it would be best to raise both the bed temperature and the air temperature in tandem in order to induce rapid evaporation of the solvent and non-solvents. While the water-heated bed is a suitable setup for a constant bed temperature, a bed with electrical-based temperature control utilising RTD probes and a PID controller with a high wattage might be the most practical way to increase and maintain the bed temperatures over a short period of time.

One parameter that needs to be quantified for the membranes discussed in this thesis is Young's modulus for PMMA membranes with and without added glycerol, water, and PEG. Attempts to measure Young's modulus were made using a Zwick Roell 2005 materials testing machine. However, the die used to cut samples to an appropriate test size caused the membranes to shatter during sample preparation. A compression-based method similar to the approach used by Wang et al. [2] might be viable, as samples do not have to be as intricately cut as with the Zwick Roell system.

Another area that would be worth investigating would be to combine water and glycerol as additives in a lacquer solution. The quickest CFT time was observed when 1 g of water was added to the lacquer mix, but this has a detrimental effect on the mechanical strength of the

membranes. Addition of glycerol as well as water might reduce these mechanical defects, as glycerol addition improved the mechanical strength overall. It can be hypothesised that addition of both water and glycerol might yield PMMA membranes with quicker CFTs and no reduction in overall mechanical properties.

Some work could also be carried out to determine if polymer chain length plays a role in the final pore morphology of PMMA membranes. Preliminary experiments indicated that the cloud point of the PMMA lacquer varies with the polymer chain length of the PMMA used, as shown in **Figure 6.1**. Further experiments could confirm whether the PMMA chain length affects the resulting membrane properties.

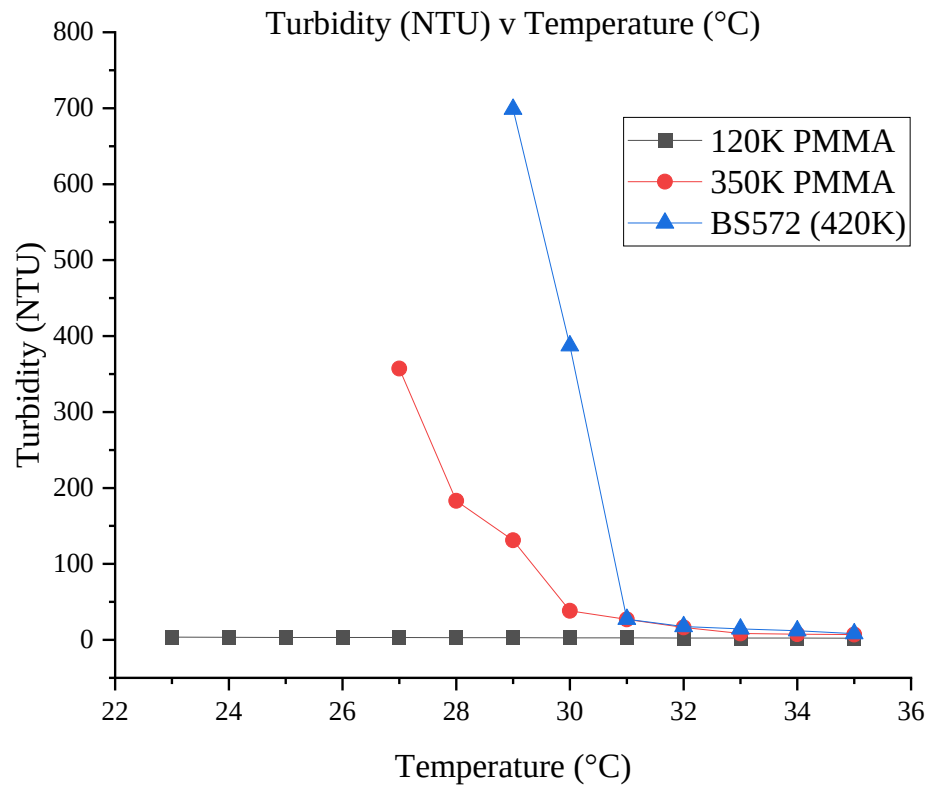


Figure 6.1: Turbidity versus temperature for 4.2% PMMA solutions using PMMA of various molecular weights.

It is possible that the PMMA packing changes with shorter polymer chain lengths and alters the gelation point (located below the cloud point). It should be possible to produce different

morphologies, as previous studies have used PMMA with molecular weights far below that of the BS572 material used for the present study [3–6].

A final area that could potentially be studied is the use of PMMA copolymers to cast membranes with hydrophilic groups such as PEO. Use of copolymers could mitigate the need to add surfactants, as the hydrophilic blocks might allow capillary flow to occur, permitting lateral flow. A number of studies have already investigated membrane fabrication with block copolymers [7] and poly(ethylene oxide)-*block*-poly(methyl methacrylate) (PEO-*b*-PMMA) membranes have been used as potential electrolytes for use in lithium ion batteries [8], and further work could investigate this potential more fully.

Final considerations for the implementation of PMMA surround cost and environmental effect. Cost may be prohibitive in gaining market traction: despite the issues previously mentioned for NC in terms of high PDI and raw material quality, a large price differential for PMMA will limit its uptake by industry. At present NC is primarily sourced from India, with costs on Indiamart ranging from ₹235 to ₹300 kg⁻¹ (equivalent to €2.70–3.50 kg⁻¹). The cost of PMMA can vary from ₹190 to ₹350 kg⁻¹ (equivalent to €2.20–3.50 kg⁻¹). Besides the raw material cost, the weight percentage loading required to produce consistent membranes is also a factor. The results here demonstrated that PMMA loading of between 2.4% and 4.2% yields a useable CFT. By contrast, NC membranes typically have a higher weight percentage loading of 10% or more, meaning that although high-molecular-weight PMMA is more expensive, less polymer may be needed from run to run.

From an environmental perspective, a number of factors need to be considered. First, the cotton used to manufacture industrial-scale NC is at present primarily produced in China and India [9]. Thus, for markets outside Asia, a significant carbon footprint is involved for raw material transport alone. By contrast, PMMA can be produced anywhere in the world as it is a synthetic polymer. Although petroleum products are used to produce PMMA, their availability in various countries globally means that PMMA manufacture can be somewhat

localised. ECO query data were used to evaluate the environmental impacts for cotton versus PMMA production. The results are summarised in **Table 6.1a–c**.

Table 6.1a: Comparison of climate change emissions for cotton v PMMA

Climate Change			
Metric	Biogenic	Fossil	Land use and Change
Unit	kg CO2-Eq	kg CO2-Eq	kg CO2-Eq
Cotton	0.0005257	1.5018	0.096904
PMMA	0.010599	7.2186	1.06E-05

Table 6.1b: Comparison of ecosystem quality for cotton v PMMA

Ecosystem Quality					
Metric	Freshwater acidification	Freshwater Ecotoxicity	Freshwater Eutrophication	Marine Eutrophication	Terrestrial Eutrophication
Unit	mol H⁺ -Eq	CTU	kg P -Eq	kg N -Eq	mol P -Eq
Cotton	0.034515	7.2236	0.001136	0.07445	0.14787
PMMA	0.039996	2.6354	0.00022177	0.0072104	0.052999

Table 6.1c: Comparison of resources used for cotton v PMMA

Resource Use				
Metric	Dissipated Water	Fossils	Land Use	Minerals and Metals
Unit	m3 water -Eq	MJ	Points	kg Sb -Eq
Cotton	104.99	14.80	233.06	1.21E-05
PMMA	1.22E+00	1.14E+02	1.84E-01	7.89E-06

The data show that cotton has a lower carbon footprint but 100-fold higher land and water utilisation, as well as a greater negative impact on ecosystem quality. Using these baseline data it might be argued that NC is a slightly greener product at present; however, such an analysis fails to include the logistics behind transport and nitrification of the raw cotton. In order to determine the true environmental footprint of both products, a full-scale life cycle

assessment should be conducted. However, from initial data it would appear that NC currently has a slight edge. Furthermore, India often experiences droughts and water deprivation. Thus, the fact that the raw material for NC requires vast amounts of water for growth [10–13] should be taken into consideration, as greater resources will be required for irrigation and water purification to meet market demands, and the supply chain could be at risk of shortages if adverse weather conditions affect a seasonal crop yield.

Taking all these factors into account, there is some merit to switching from NC to PMMA for membrane fabrication, although there will be a trade-off in terms of carbon emissions according to current utilisation patterns. However, these may be balanced by the localisation of PMMA production and the shortening of supply chains and the reduction in water consumption required for cotton production in deprived countries such as India.

In conclusion, the merits of PMMA as a replacement for NC for membrane fabrication warrant further investigation.

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