

Porous Matrimid[®] Support Membranes for Organic Solvent Separations

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Abstract

Porous Matrimid[®] polymeric membranes were developed as supports for thin film composites (TFCs) of dense, selective polymers to target organic solvent separations. Selective polymers form dense membranes and must be thinly coated on porous supports to obtain high permeances (pressure-normalized fluxes) of target solvents. The goal of this work was to develop support membranes that demonstrated excellent stability in organic solvents and sufficient porosity to allow toluene permeances of 60-200 Lm⁻²h⁻¹bar⁻¹ such that a composite has permeance of 0.1-1 Lm⁻²h⁻¹bar⁻¹. A final objective was to quantify the effects of production conditions on membrane morphology and performance. Polymer ‘dopes’ (homogeneous polymer solutions) of Matrimid[®] containing varying compositions of solvent and non-solvent were cast using the phase inversion technique. The resulting flat membranes were then crosslinked to prevent dissolution in harsh solvents. The desired permeance was achieved with a precise control over the dope compositions and production conditions. The impact of several casting parameters such as co-solvent evaporation time, ambient humidity, and post-processing procedures were studied. Generally, a decrease in permeance was observed as the drying time prior to phase inversion was increased. Average permeance at the optimized dope composition was 76.4 Lm⁻²h⁻¹bar⁻¹, with a standard deviation of 62.5 Lm⁻²h⁻¹bar⁻¹. The effect of different crosslinkers on membrane swelling and permeability was quantified, with 1,6-hexanediamine emerging as the most suitable crosslinker. Gas porosimetry was used to determine surface pore size, which was found to generally increase with permeance.

Introduction

Approximately 15% of US energy consumption is spent in industrial materials separations. Membrane separations would use 90% less energy than distillation,¹ offering a significant opportunity for energy reduction in oil refining and petrochemicals. The development of membrane separation processes is an active area of industrial research, offering many advantages over traditional column separations. Membranes can offer lower-maintenance operation, do not require phase changes, and can run continuously.² Extensive research has advanced some membrane operations, such as water purification through reverse osmosis and gas separations. However, the field of organic solvent separations for scalable applications in oil refining, pharmaceuticals, and petrochemicals has been less explored due to the unique challenges posed by

organic solvents, including harsh physical properties and similarities between molecules being separated.^{3, 4}

Membranes may be made from active polymers that separate organic solvents by molecular size and shape, or organic solvents from large solutes. Examples of such materials are polymers of intrinsic microporosity (PIMs) which are characterized by twisted hydrocarbon rings around a spirocenter and a rigid polymer backbone.⁶ Monolithic membranes for organic solvent separations can be produced, but the permeances are usually slow, hindering the lab-scale separation performance analysis and causing productivity issues for large-scale operations.⁵ Furthermore, a stand-alone thin layer of selective polymers would be too delicate for experimental testing at high pressures. It is necessary for the scope of the research to develop a porous support membrane to provide mechanical stability to the thin film while maintaining a high flux.

Previous studies have correlated various casting and processing conditions with particular membrane properties. However, these results can be difficult to replicate and there is limited information on the impact of different crosslinkers on membrane swelling effects. The development of a reproducible support structure for selective polymers is needed to efficiently test a variety of active polymers and develop a portfolio of separation capabilities. As such, thin film composites comprised of thin, selective polymer layers coated on porous support structures have been investigated. Support layers can be made of polyimide membranes, such as Matrimid®, fabricated into porous, integrally skinned asymmetric membranes (ISAs) through phase inversion. The ISA structure is targeted to provide a dense surface on which to evenly coat an active polymer while providing mechanical support from a porous substructure. A process to make ISAs was developed by Sun et al., although the phase inversion technique of precipitating membranes has existed since the 1970s. Sun et al. reports development of an integrally skinned asymmetric membrane with high permeance for organic separations using Matrimid® supports crosslinked with 1,6-hexanediamine. Crosslinked polyimide membranes show improved resistance over previously explored polymers.⁷ Liu et al. identified diamines as a suitable crosslinking agent for polyimides,⁸ and the reaction mechanism was determined by Shao et al.⁹

Matrimid® was identified as a suitable material for supports due to its flexibility in the dry state, easy processability, and chemical compatibility with the active polymers of interest. Key targets for Matrimid® support membranes are stability in organic solvents and toluene permeance of 60-200 Lm⁻²h⁻¹bar⁻¹ such that the support does not dominate the solvent permeance in the thin film composite. A final objective was to determine the effects of varying casting conditions on

membrane performance and morphology. The desired permeance was achieved for a narrow range of dope compositions. Surface pore size was also quantified and correlated with permeance to determine a maximum optimum permeance for a required surface pore size. Despite mechanical resistance to hexane and toluene and sufficient permeability, swelling in organic solvents and support reproducibility are existing challenges.

Literature Review

Many factors impact polymeric membrane performance, including composition, processing conditions, and post-processing treatment. Previous research has quantified many of these relationships. Polyimides such as Matrimid® have been prepared as integrally skinned asymmetric membranes (ISAs), similar to the support structures studied in this research.

Marchetti et al. described the process for developing ISAs made from commercially available polyimides for organic solvent separations. An ISA is traditionally fabricated by casting a controlled thickness of a dope, a homogenous polymer solution containing solvents and non-solvents, on a glass plate. This layer of dope is then phase inverted in a bath of non-solvent such as water. Dope composition and casting conditions, including drying time, gas stream velocity, temperature, and solvent exchange fluid, affect membrane properties. As solvent evaporates during casting, the top of the membrane collapses and a dense polymer skin layer is formed at the surface, which causes decreased solvent permeance. The substructure is porous, as it takes longer for the solvent to evaporate through the dense layer, leaving larger pores. The skin layer is formed from both evaporation of volatile solvent from the dope and the wet phase inversion step. When submerged in water, the membrane rapidly precipitates into two phases: the polymer matrix and liquid in the pores. Due to the direct contact with water, the top precipitates rapidly and forms a dense layer that slows water diffusion such that the rest of the solution precipitates slowly, forming a more porous membrane.³ Pinnau et al. studied the formation of the skin layer with findings consistent to those listed above, adding that phase inversion alone is not recommended for making a defect-free skin layer.¹⁰ A balance must be found between the drying and phase inversion steps to create a thin, defect-free skin layer and porous substructure.

Dope compositions are determined through trial and error and determination of the two-phase region. Xu et al. found a narrow operating window in which to formulate the dope.¹¹ Clausi et al. and others have correlated higher volatile solvent content with a thicker skin layer and decreased gas permeance.¹² Marchetti et al. showed that higher polymer content in the dope leads

to a thicker, denser skin layer, yielding higher selectivity but lower permeability.³ Lithium nitrate is sometimes added to increase dope viscosity and aid phase separation. This allows polymer concentration to be reduced, reducing the skin layer thickness.¹¹

Several studies have shown that smaller air gaps (shorter drying time) yield thinner skin layers in hollow fiber membranes,^{11, 12} Using a higher velocity gas stream for forced convection of solvent evaporation leads to a higher concentration of polymer in the skin layer.¹⁰ The drying solvent also influences skin layer thickness and permeance. Clausi et al. found that when the final solvent exchange fluid before drying was water, lower permeance and higher skin thickness were reported, while solvent exchanging with methanol and hexane before drying increased pore size and reduced skin layer thickness. This is believed to be caused by the strong capillary forces exerted by water on pore walls.¹²

Polyimides such as Matrimid® are not inherently resistant to organic solvents, thus, crosslinking steps must be taken to eliminate dissolution in harsh organic solvents. Crosslinking can also be used to reduce swelling in organic solvents and prevent changes in the membrane morphology that may crack the thin selective polymer layer during swelling or drying. There are many methods employed to crosslink polyimides summarized by Vanherck et al., including thermal, UV, and chemical crosslinking with diols or diamines.¹³ Thermal crosslinking will break down the membrane's inherent porous structure, and Matrimid® lacks the requisite carboxylic acid groups for diol crosslinking. Diamine crosslinking has been found as the most effective technique for the application. The diamine crosslinking reaction mechanism was investigated by Shao et al. They determined that the nucleophilicity of the diamine determines the rate of reaction. The mechanism involves conversion of the imide bonds to amide bonds bridging polymer chains. Furthermore, they found that use of a bulky diamine resulted in lower degrees of crosslinking. This could impact membrane stability, swelling, and plasticization effects.⁹ Shao et al. found that time spent crosslinking with EDA significantly impacts membrane structure and increases gas selectivity.¹⁴

Polyimides tend to swell in organic solvents. Ideal polymeric membranes are glassy, with a high glass transition temperature. Crosslinking can be used to achieve the desired glassy state. Hillock and Koros used diols to crosslink polyimides containing a carboxylic acid group prior to casting the membrane. They found superior membrane performance and plasticization resistance as a result.¹⁷ Conversely, Shao et al. found that EDA crosslinking caused increased plasticization due to disruption of polymer chains. They found that thermal annealing was required to eliminate

plasticization.¹⁴ Vanherck et al. found that crosslinking with XDA reduced plasticization and swelling.¹⁶ Several studies have found thermal annealing to be effective in elimination of plasticization, however, this technique breaks down the asymmetry of the membrane⁸ and alters the structure unfavorably for this work. It is necessary to develop a membrane with reduced swelling and plasticization, as well as resistance to organic solvents and retention of the asymmetric porous structure.

Modeling molecular transport through a membrane is vital to determine the surface pore size of the Matrimid® supports. Bowen and Welfoot modeled penetrant transport with the pore-flow model to correlate the flux and rejection with the pore size distribution.¹⁸ Gas molecules are transported through the porous membrane by pressure-driven flow and Knudsen diffusion, a mechanism in which the molecules have significant interaction with the pore walls. The total flowrate is the sum of these contributions. In gas porosimetry, the gas permeance of a membrane is measured at a range of different pressures. The slope of the resulting graph corresponds to pressure-driven flow, and the y-intercept represents Knudsen flow as shown in Figure 1.

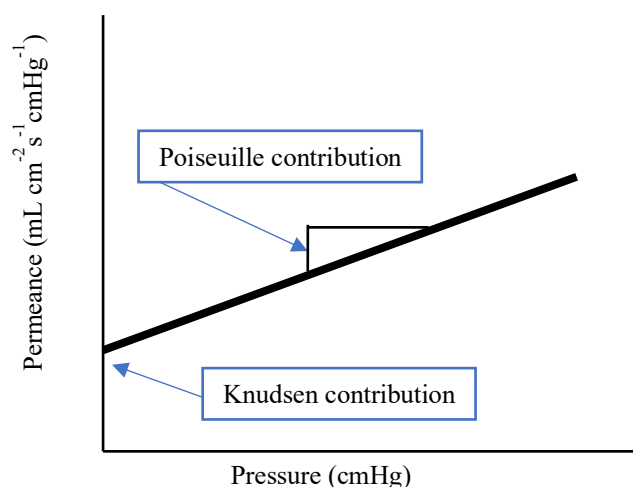


Figure 1. Determination of Poiseuille and Knudsen flow.¹⁹

The mean pore radius can be found by taking the ratio of these values and substituting mean molecular speed and viscosity.¹⁹

A key goal of this study was to establish a reproducible procedure for making support membranes, eliminating variables that have caused performance inconsistency. This project aimed to reduce or rigorously quantify swelling effects through the identification of the most appropriate diamine based on literature findings. Once key permeability targets were met, gas porosimetry was used to determine the pore sizes of the skin layer.

Materials and Methods

Materials

Matrimid® was obtained from Huntsman International (The Woodlands, TX). Toluene, anhydrous tetrahydrofuran, N-methyl-2-pyrrolidone, and ethanol were obtained from Sigma Aldrich (St. Louis, MO) and used as received. Lithium nitrate was obtained from Alfa Aesar (Ward Hill, MA). Methanol and hexane were obtained from VWR (Radnor, PA) and used as received.

Dope synthesis

Prior to dope synthesis, powder Matrimid® and lithium nitrate (LiNO_3) were dried overnight at 110°C and 30 mmHg vacuum. Dopes were composed Matrimid®, LiNO_3 water, ethanol, THF, and NMP to total 15 g. To minimize water absorption from the atmosphere and altering the water content in the dope, LiNO_3 was always measured out first and solvents added immediately after. Vials were sealed with solvent tape then placed on a roller under a heating lamp until polymer was completely dissolved and the solution was uniform. Dopes were removed from the roller and allowed to stand upright overnight to degas the dope.

Blade Casting

Once degassed, dopes were ready for casting. A glass plate and 10 mil casting knife were cleaned and dried. The plate was placed on an automatic blade coater set to move the knife uniformly at 20 mm/s. Dope was poured uniformly across the plate in front of the knife, then the apparatus moved the knife and dope across the glass, creating a uniform sheet of polymer solution. The material was allowed to stand and dry for a controlled period of time, during which volatile solvents evaporated and slowly began the membrane phase change. Over the course of the next 10 seconds, the glass plate was transferred toward a DI water bath at room temperature. The plate was placed in the bath and the membrane solidified quickly, delaminating from the plate. Temperature and humidity were closely monitored during casting.

Post Processing

Membranes were left submerged in a water bath for 24 hours to ensure complete removal of THF and NMP from the material. After 24 hours, solvent was exchanged with methanol three times and left for one hour after each exchange. The process was repeated with hexane. The membranes were air dried for three hours protected from dust, then oven dried overnight at 110°C and 30 mmHg vacuum. Circular coupons were cut out, noting the relative location on the larger sheet. Finally, 5 wt% crosslinking solution of either 1,6-hexanediamine or para-xylylenediamine

in methanol was prepared. The membranes were submerged in crosslinking solution for 24 hours. Crosslinked membranes were then rinsed three times with methanol with an hour between each rinse. After removing any remaining crosslinker, membranes were ready for testing.

Dead-End Filtration

Membranes were cut to fit a circular, steel backing and 4 cm diameter O-ring. These were set-up in a dead-end permeation cell (Steriltech Corporation). The cell was sealed for leaks, filled with 200 mL toluene, then pressurized with 50 psi nitrogen. After 25 mL toluene permeated through the membrane, the flux of the permeate was measured.

Data Analysis

Permeance is defined as the pressure normalized flux, calculated as

$$P = \frac{J}{\Delta p} = \frac{\text{Volume}}{\text{Surface area} \cdot \text{time} \cdot \text{Pressure}} \quad (1)$$

with units of $Lm^{-2}h^{-1}bar^{-1}$. Membrane permeances were evaluated for statistical significance and minimizing standard deviation.

Gas Porosimetry

Gas porosimetry was used to calculate the average surface pore size of Matrimid® supports. Membranes were set up in a dead-end cell used to measure gas flux through the membrane. Nitrogen and helium flowed through the membranes at 35°C. Flux measurements were taken in triplicate at five pressures between 1 and 20 psi. The permeance was plotted against average pressure in order to determine the average surface pore size.

Gas flux through porous membranes occurs through pressure driven Poiseuille flow and Knudsen diffusion. Poiseuille flow, corresponding to the slope of permeance over pressure, can be represented

$$\frac{\dot{Q}_{\text{Poiseuille}}}{p_{\text{avg}}} = \frac{\varepsilon \cdot r_p^2}{8 \cdot \mu \cdot \tau \cdot R \cdot T \cdot l} \quad [2]$$

And Knudsen flow, found from the intercept, is

$$\dot{Q}_{\text{Knudsen}} = \frac{2 \cdot \varepsilon \cdot r_p \cdot \bar{U}}{3 \cdot \tau \cdot R \cdot T \cdot l} \quad [3]$$

with μ as viscosity and \bar{U} as average molecular velocity. Taking the ratio of these two contributions and substituting μ and \bar{U} yields r_p , average surface pore size.

Results and Discussion

Matrimid[®] was dissolved in solvent of varying compositions to form dopes, then processed into integrally skinned asymmetric membranes. Support membranes require small surface pores in order to create an even layer of selective polymer on the surface, however, should not hinder solvent flux. Therefore, the skin layer should be thin, with the porous substructure providing the bulk of the mechanical support. SEM imaging reveals this structure, as shown in Figure 2.

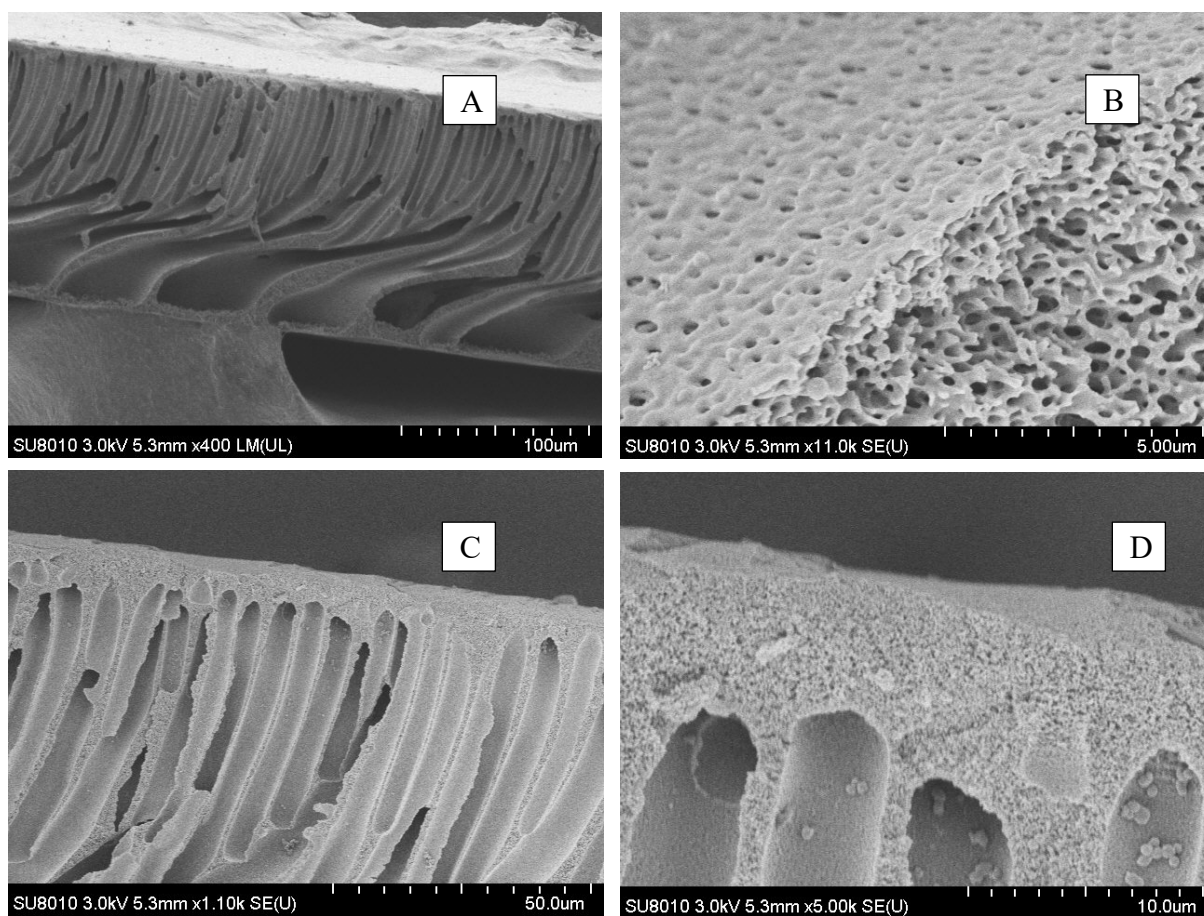


Figure 2. SEM imaging of a porous support with dope composition 16% Matrimid, 10% THF, 69% NMP. A) Cross section of entire support. B) Surface pores. C) Cross section with porous substructure. D) Dense skin layer.

Surface pore sizes can be approximated from the image as just less than 500 nm diameter. The wider channels beneath are approximately 5 μm . The membrane pictured was formed from a 16% Matrimid[®], 10% THF, 69% NMP dope, and its permeance was 65.7 $\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$ in toluene.

Effect of drying time on permeance

The effect of drying time, or solvent evaporation time, before phase inversion was studied. It was hypothesized that increased drying time would result in greater solvent evaporation and subsequent polymer collapse into a more dense structure. This was generally observed, with lower permeances seen at longer drying times as shown in Figure 3.

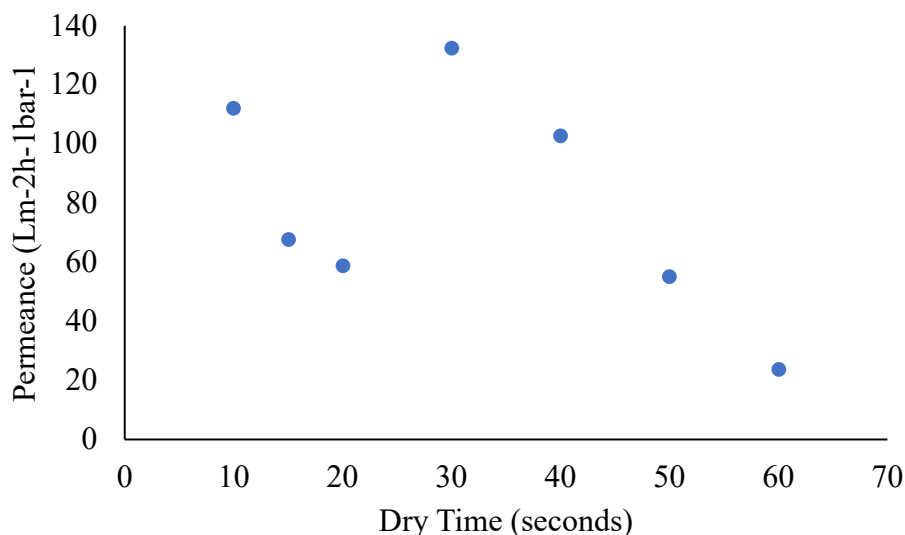


Figure 3. Effect of drying time on permeance.

At drying times under 20 seconds, a higher variability in permeance was observed. Membrane batches dried for 20 seconds had high standard deviations, potentially due to uneven phase inversion when submerged in water. Solvent evaporation may contribute more to phase inversion at longer drying times when the membrane structure is closer to solidification before submerging in the water bath. Water submersion plays a larger role in solidifying the membrane at low drying times because the membrane is still a one-phase solution and pores are not fully formed. This process is more aggressive and less controlled if the pores are nascent in their formation, leading to variation and high standard deviation. Furthermore, the membranes delaminate unevenly from the edges to the center, further contributing to variation at low dry times. Further experimentation is needed to more rigorously quantify this trend.

Effect of Tetrahydrofuran content on permeance

The effect of tetrahydrofuran (THF) content in the dope on permeance was studied. It was hypothesized that increased THF content would result in decreased permeance due to more rapid evaporation of the low-boiling point solvent and subsequent collapse of surface polymer into a

dense skin layer. Dopes were made with varying amounts of THF and N-methylpyrrolidone (NMP) and constant amounts of Matrimid® (16%), lithium nitrate (1%), ethanol (3%), and water (1%) over several batches. These dopes were cast, phase inverted, and post-processed, maintaining as constant conditions as possible. Average permeance for dopes with 10%, 11%, and 13% THF are shown in Figure 4 as 76.4 ± 21.3 , 54.4 ± 57.9 and 17.6 ± 8.9 $\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$, respectively.

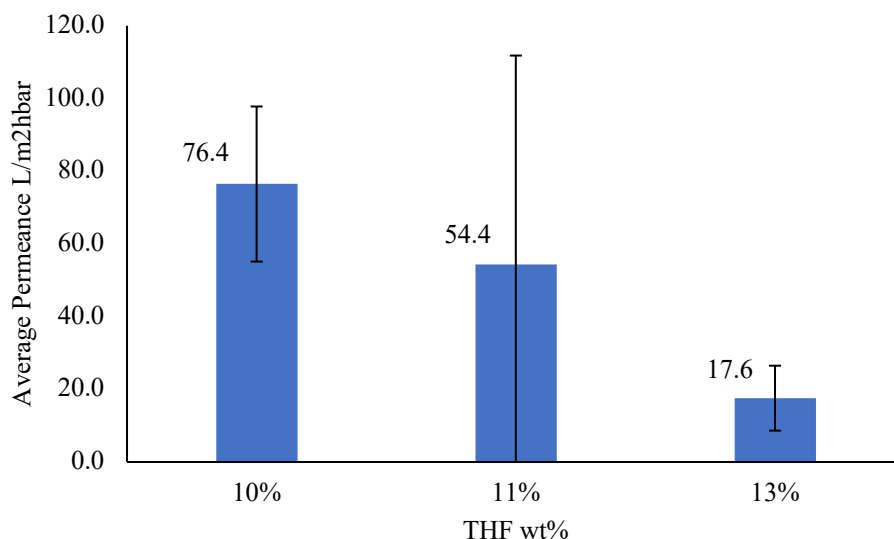


Figure 4. Effect of THF content on average permeance, with 95% confidence intervals shown.

The averages shown in Figure 4 indicate that increasing THF content relative to NMP content results in lower permeance. The large error on 11 wt% THF is because few samples were available for analysis. THF is much more volatile than NMP, resulting in rapid solvent evaporation and a more dense skin layer. Permeance may be easily tailored by altering dope composition rather than relying on the inconsistent impact of casting conditions, allowing support permeance to be varied as needed for target applications.

Crosslinker Comparison

Despite mechanical resistance to solvents and good permeance, membrane swelling in organic solvents is an existing issue for supports for polymer spin coating applications. The size difference between wet and dry membranes is significant. If selective polymers are coated on wet Matrimid®, cracking may occur as the support layer dries. It was desired to reduce swelling effects through diamine crosslinking, which reduces plasticization. Ethylenediamine, 1,6-hexanediamine, and para-xylylene diamine were used to crosslink both Matrimid® dense films and porous supports at 2.5 and 5 wt% in methanol. The mass and diameter of dry and wet states were compared, as

shown in Figure 5. These measurements were difficult to obtain due to rapid methanol evaporation and shape change, however, the data are generally reflective of swelling tendencies.

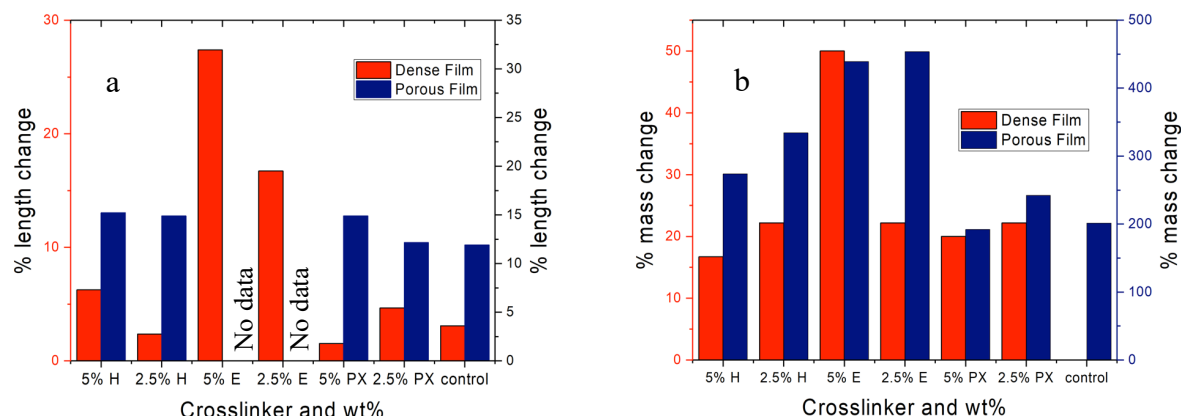


Figure 5. Swelling effects on a) diameter change and b) mass change. Ethylenediamine-crosslinked membranes became too brittle to obtain diameters, and two data points are missing as indicated.

Membranes crosslinked in 1,6-hexanediamine and para-xylylenediamine showed similar diameter and mass changes between dry and wet states. Ethylenediamine membranes had a large difference between the wet and dry state. Dry membranes shrank and curled, becoming too brittle to manually handle and were unsuitable for spin coating. Other crosslinked membranes retained a flat shape and flexibility, as shown in Figure 6.



Figure 6. Dry membranes crosslinked with a) ethylenediamine, b) 1,6-hexanediamine, and c) para-xylylenediamine

Ethylenediamine is a short molecule compared to 1,6-hexanediamine and para-xylylenediamine, resulting in crosslinks that disrupted the pore structure and made the membrane brittle. As a result, 1,6-hexanediamine was selected for subsequent use. There was minimal difference in the performance between 1,6-hexanediamine and para-xylylenediamine.

Surface Pore Size Quantification

Gas porosimetry was used to calculate the surface pore size of supports to determine the relationship between surface pore size and toluene permeance. It was hypothesized that the skin layer dominates solvent flux, so smaller surface pores would inhibit flux. This trend generally held true, and toluene permeance is observed to increase with surface pore size, as shown in Figure 7.

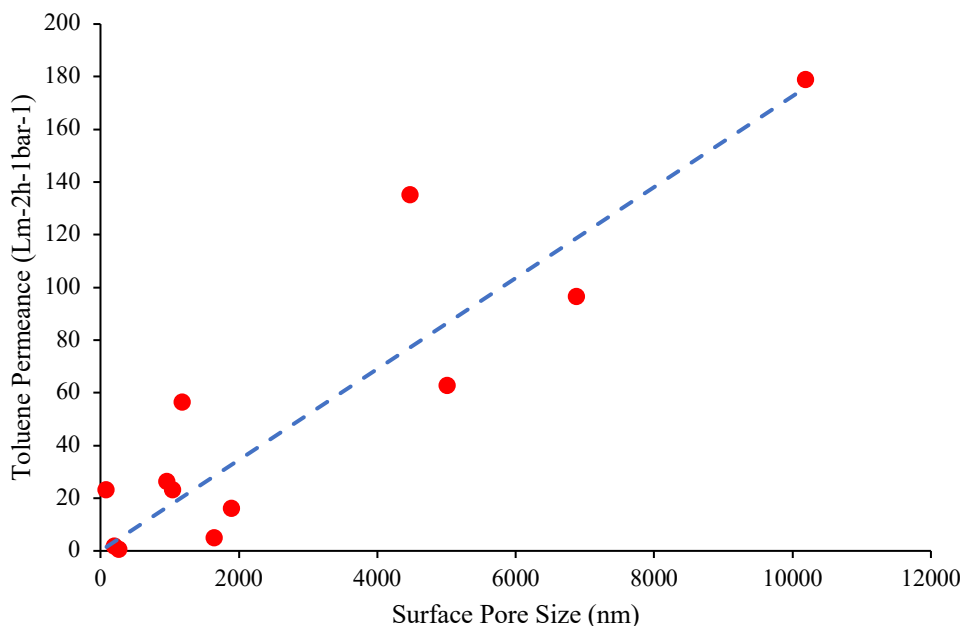


Figure 7. Toluene permeance and surface pore size.

Figure 7 shows a tradeoff between small surface pore size and permeance. The R-squared for this relationship was 0.8. Smaller pore sizes have the benefit of reducing swelling and thin film collapse on the support, however, high permeance is necessary to obtain product. This graph can help determine the maximum permeance if a particular pore size is stipulated for a certain thin film composite product.

Error and Reproducibility

Support reproducibility is a remaining issue. Variation between and within batches stemmed from a variety of sources, including solvent evaporation time and deviations in post-processing procedures. During early experimentation, drying after phase inversion was not carefully controlled, and membranes were allowed to air dry to varying degrees over an unspecified period of time. Evaporation of water was hypothesized to damage pore structure due to its high surface tension. As a result, the pore structure varied with extent of drying after phase inversion.

Exact dope formulation is essential to establishing reproducibility. Minor additions of water content can make a large impact on permeance. Figure 8 compares the average permeance of samples made with anhydrous and non-anhydrous NMP.

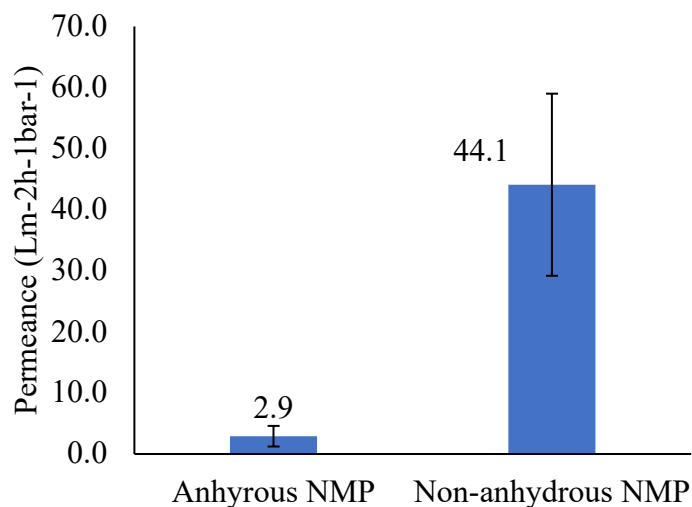


Figure 8. Effect of NMP quality on permeance with 95% confidence intervals shown.

Supports made with anhydrous NMP had an average permeance of $2.9 \pm 1.7 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$, significantly lower than previously manufactured samples with non-anhydrous NMP with an average permeance of $44.1 \pm 14.9 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$. Supports were processed similarly across trials. The low permeance results were observed after higher-quality NMP was used due to reduced water content in the NMP and resultant dope.

Casting humidity also affects membrane permeance. It was hypothesized that casting in high-humidity environments would result in increased permeance due to greater amount of non-solvent in the atmosphere. The data thus far follow the hypothesis, as shown in Figure 9.

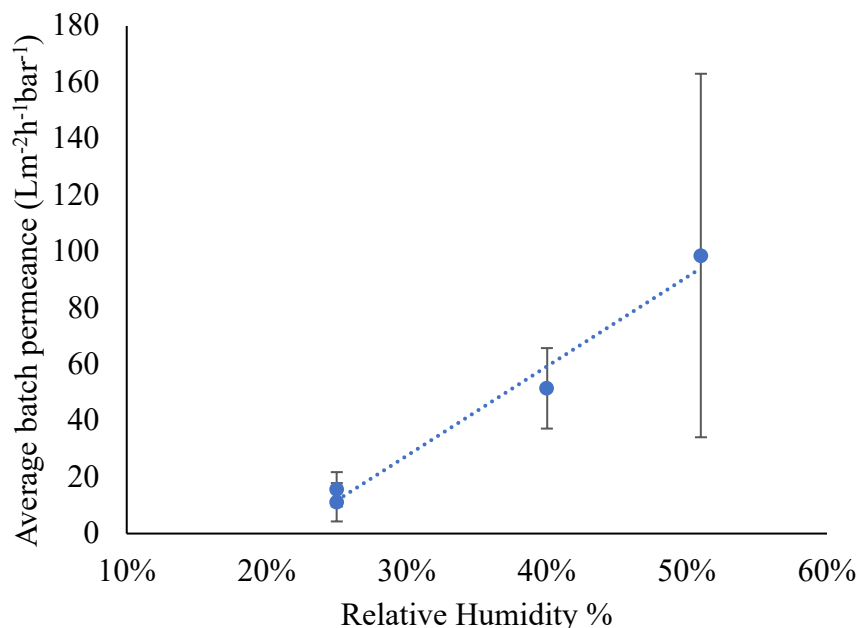


Figure 9. Permeance vs. relative humidity during casting with 95% confidence intervals shown.

Figure 9 compares membrane permeances of similarly processed batches cast in different humidity environments due to weather changes. Average permeance of the batch is shown to increase with humidity, with an R^2 of 0.98.

Conclusions and Recommendations

Desired permeance was achieved with dopes composed of 10% THF, 69% NMP, 1% water, 1% lithium nitrate, 3% ethanol, and 16% Matrimid with an average permeance of $76.4 \pm 21.3 \text{ Lm}^2\text{h}^{-1}\text{bar}^{-1}$. Increased THF content in the dope results in lower permeance, allowing for customizable support permeance for different applications. 1,6-hexanediamine and para-xylylene diamine were identified as suitable crosslinkers, while use of ethylenediamine made membranes brittle and more susceptible to swelling. A correlation between permeance and average surface pore size was found, making it possible to find a maximum permeance for a target surface pore size.

Further experimentation is required to more rigorously establish support reproducibility and eliminate production variables. Careful dope formulation and adherence to specified procedures will reduce experimental error. If anhydrous NMP is used, dopes should be reformulated to include more water and retain high permeance. Longer solvent evaporation times

should be investigated. Casting on porous backing may prevent uneven delamination from the glass plate during phase inversion. Further investigation is needed to determine the optimum surface pore sizes for the target application, balancing the tradeoffs between swelling tendencies and permeance and surface pore size. Less hazardous solvents should be investigated to improve safety and potential for industrial scale-up. Finally, supports should be tested with a variety of selective polymers to establish their versatility.

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