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D5.2 Bi-soft Membrane

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1 EXECUTIVE SUMMARY

This document presents the deliverable D5.2 “Bi-soft Membrane” of the EIC Pathfinder Open project BioMembrOS. It details the protocols established for the production of bi-soft segment polyurethane (PU)-based flat sheet membranes, specifically with symmetric dense and integral asymmetric cross-sectional structures. Additionally, it presents the gas permeation results for gases of interest, namely oxygen (O₂) and carbon dioxide (CO₂). This deliverable sets guidelines for producing bi-soft segment PU-based membranes and evaluates their gas permeation performance in comparison to thermoplastic polyurethane (TPU)-based membranes also developed in the scope of the project.

2 KEYWORD LIST

Artificial respiration

Bi-soft segment polyurethane-based membranes

Blood oxygenator

Casting solution

Deliverable

EIC Pathfinder Open

Gas permeation

Integrally asymmetric membrane

Mixed matrix membrane

Metal-organic framework

Nanoparticle dispersion

Symmetric dense membrane

Thermoplastic polyurethane

3 LIST OF ACRONYMS

ACET	Acetone
DEE	Diethyl ether
DMF	Dimethylformamide
EIC	European Innovation Council
IST	Instituto Superior Técnico
MMM	Mixed matrix membrane
MOF	Metal-organic framework
TMP	Transmembrane pressure
TPU	Thermoplastic polyurethane
PPO	Poly(propylene oxide)
PU	Polyurethane
PUR	Polyurethane-based prepolymer
PCL	Polycaprolactone

4 INTRODUCTION

In this document, the deliverable D5.2 “Bi-soft Membrane” for the EIC Pathfinder Open project BioMembrOS is presented. The production of bi-soft segment polymers was achieved by reacting a poly(propylene oxide)(PPO)-based prepolymer with three isocyanate terminal groups (PUR) with poly(caprolactone-diol) (PCL-diol) at room temperature conditions. Incorporating the PCL soft segment significantly enhances hemocompatibility, particularly by reducing membrane surface-platelet adhesion and activation.

This deliverable outlines the methodology used to synthesize the bi-soft segment polymers and respective membrane casting solutions, enabling the production of bi-soft segment flat sheet membranes (both symmetric dense and integrally asymmetric). These membranes were developed for the gas permeation of target gases, such as O₂ and CO₂, with potential application in next-generation artificial respiration devices (i.e., blood oxygenators). The described methodology is designed to be adaptable, allowing customization of the PCL content in the final bi-soft segment polymer as required.

A comparison is conducted between bi-soft segment membranes and TPU-based membranes developed within the project to determine which polyurethanes offer superior O₂ and CO₂ permeation performance. This evaluation aims to identify the most suitable class of polyurethanes to produce mixed matrix membranes (MMMs) containing metal-organic frameworks (MOFs) as fillers.

5 METHODOLOGY

5.1 Production of PUR-based symmetric dense membranes: polymer/solvent ratio optimization

To optimize the polymer/solvent ratio for producing symmetric dense membranes, casting solutions were prepared by dissolving the PUR prepolymer FABRICOL AG 202 (FabriRes – Produtos Químicos, S.A.) in dimethylformamide (DMF, ≥99.5%, Fisher Chemical). The target was to achieve a dynamic viscosity between 3 and 10 P at 30 °C, ensuring the solution could be easily spread onto a glass casting plate to obtain a symmetric dense membrane.

Firstly, the PUR prepolymer was weighed into a flat-bottom flask. DMF was then added, along with a 40 mm triangular magnetic stirring bar. The dissolution was carried out under an inert nitrogen atmosphere to prevent the reaction between isocyanate terminal groups of the prepolymer and atmospheric moisture. The dissolution process was conducted at room temperature (22 ± 2 °C) for 2 hours, with the flask being sealed using a Suba-Seal® septum. After dissolution, the solution was left still for 1 h to allow gas bubbles to dissipate before casting. Each casting solution was spread onto a glass plate using a 250 µm Gardner knife and left to dry in air at room temperature for 48 h. Immediately after the spreading process, the remaining flask content was placed under an inert atmosphere so that the sample was not compromised before viscosity measurements.

Table 1 shows the compositions of the tested casting solutions. Dynamic viscosity was measured immediately after their casting using a REL cone-and-plate viscometer, with triplicate measurements performed at 30 °C. After assessing the viscosity of the casting solutions, the optimal polymer/solvent ratio was determined to be 80%/20%.

Table 1: Tested casting solution compositions for PUR prepolymer to produce symmetric dense membranes.

Casting solution PUR%-DMF%	PUR (wt.%)	DMF (wt.%)	Dyn. viscosity at 30 °C (P)
Casting solution 100-0	100	0	80
Casting solution 85-15	85	15	7.8
Casting solution 80-20	80	20	4.0
Casting solution 65-35	65	35	0.6
Casting solution 60-40	60	40	0.4
Casting solution 15-85	15	85	< 0.1
Casting solution 10-90	10	90	< 0.1

Figure 1 shows the symmetric dense membranes obtained from the casting solutions with dynamic viscosities exceeding 1 P.

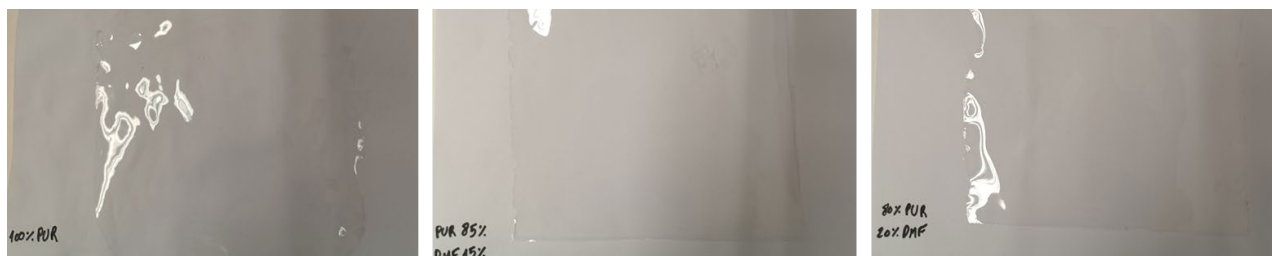


Figure 1: The obtained symmetric dense PUR-based membranes from selected PUR-DMF casting solutions: PUR 100%-DMF 0% (left), PUR 85%-DMF 15% (center), and PUR 80%-DMF 20% (right).

5.2 Production of PUR-based integrally asymmetric membranes

To produce integrally asymmetric membranes, a pair of solvents is required to prepare the casting solution. The chosen solvents were DMF and the more volatile diethyl ether (DEE, ≥ 99.5 , Fisher Chemical). During the casting, the time-controlled evaporation of DEE at the membrane surface exposed to air facilitates the formation of a thin dense layer at the top of a porous support layer. Since the dense layer thickness primarily determines resistance to transport in gas permeation applications, integrally asymmetric membranes achieve a higher total flux compared to symmetric dense membranes.

Using a polymer/solvent ratio of 80%/20%, an integrally asymmetric membrane was produced with a solvent mixture of DMF and DEE, with a DMF/DEE ratio of 3:1. The PUR prepolymer was weighed into a flat-bottom flask, followed by the sequential addition of DMF and DEE, along with a 40 mm

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triangular magnetic stirring bar. The dissolution was carried out under an inert nitrogen atmosphere to prevent the isocyanate terminal groups of the prepolymer from reacting with atmospheric moisture. The dissolution process was conducted at room temperature (22 ± 2 °C) for 2 hours, with the flask being sealed using a Suba-Seal® septum. After dissolution, the solution was left still for 1 h to allow gas bubbles to dissipate before casting. The casting solution was spread onto a glass plate using a 250 µm Gardner knife and the membrane was exposed 1 min to the atmosphere. Following the phase inversion technique, the glass plate was submerged in a coagulation bath of deionized water at room temperature for 24 hours. In this case, water acts as a nonsolvent and exchanges with DMF. Afterward, the membrane was removed from the glass plate and left to dry at room temperature.

Figure 2 shows the obtained integrally asymmetric membrane.

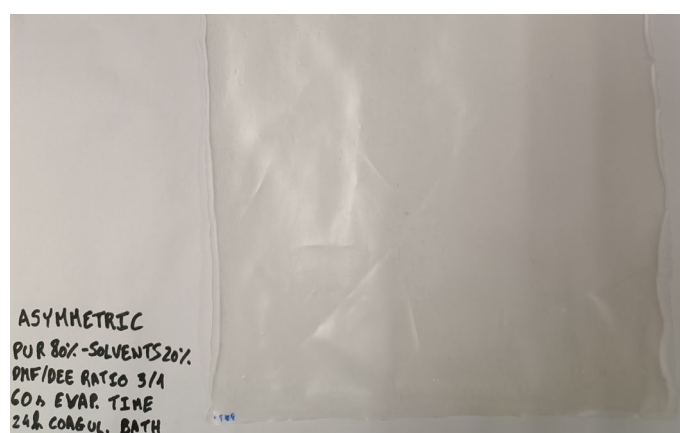


Figure 2: The obtained integrally asymmetric PUR-based membrane (DMF/DEE ratio of 3/1 and 1 min of exposure time).

5.3 Production of bi-soft segment PUR/PCL-based membranes

Bi-soft segment symmetric dense and integrally asymmetric membranes were prepared with a PUR/PCL ratio of 95/5 (wt.%).

To produce the symmetric dense membrane, a polymer/DMF ratio of 80%/20% was used for the casting solution. The PUR prepolymer was weighed into a flat-bottom flask, followed by the sequential addition of PCL and DMF, along with a 40 mm triangular magnetic stirring bar. Dibutyltin dilaurate (>95%, TCI) was used as a catalyst, with one drop being added to the reactional medium. The polymerization reaction was carried out under an inert nitrogen atmosphere to ensure the free isocyanate terminal groups of the PUR prepolymer reacted with the PCL segments rather than with atmospheric moisture. The dissolution process was conducted at room temperature (22 ± 2 °C) for 2 hours, with the flask being sealed using a Suba-Seal® septum. After the reaction was stopped, the casting solution was left still for 1 h to allow gas bubbles to dissipate before casting. The solution was spread onto a glass plate using a 250 µm Gardner knife and left to dry in air at room temperature for 48 h.

To produce the integrally asymmetric membrane, a polymer/solvent ratio of 80%/20% was used for the casting solution, along with a DMF/DEE ratio of 3:1. The PUR prepolymer was weighed into a

flat-bottom flask, followed by the sequential addition of PCL, DMF, and DEE, along with a 40 mm triangular magnetic stirring bar. Dibutyltin dilaurate was again used as a catalyst, with one drop being added to the reactional medium. The polymerization reaction was carried out under an inert nitrogen atmosphere to ensure the free isocyanate terminal groups of the PUR prepolymer reacted with the PCL segments rather than with atmospheric moisture. The dissolution process was conducted at room temperature (22 ± 2 °C) for 2 hours, with the flask being sealed using a Suba-Seal® septum. After the reaction was stopped, the casting solution was left still for 1 h to allow gas bubbles to dissipate, followed by 5 min in an ultrasound bath at room temperature to remove further gas bubbles. The casting solution was spread onto a glass plate using a 250 µm Gardner knife and the membrane was exposed 1 min to the atmosphere. Following the phase inversion technique, the glass plate was submerged in a coagulation bath of deionized water (non-solvent) at room temperature for 24 hours. Afterwards, the membrane was removed from the glass plate and left to dry at room temperature.

Figure 3 shows the obtained bi-soft segment membranes.

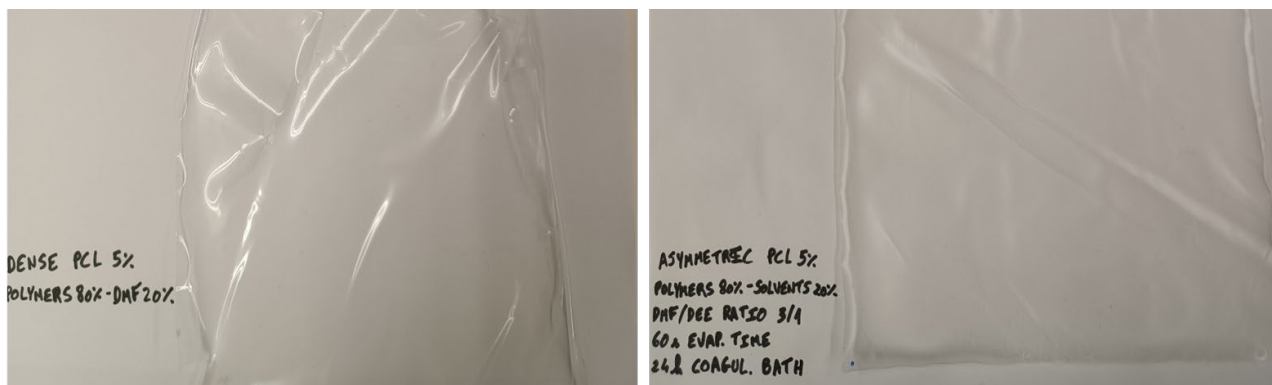


Figure 3: The obtained bi-soft segment symmetric dense (left) and integrally asymmetric (right) PUR/PCL-based membranes.

5.4 Production of TPU-based membranes

To produce the TPU-based symmetric dense membrane (casting solution TPU 10%-DMF 90%), 45.00 g of DMF was weighed in a 100 mL Erlenmeyer flask with a screw cap. A 40 mm triangular magnetic stirring bar was added, and the mixture was stirred at 600 rpm using a magnetic stirrer at room temperature. Next, 5 g of the Elastollan® 1170 A 10 000 TPU was gradually added to the flask under continuous stirring, after which the flask was sealed with the screw cap. After 1 hour, the stirring speed was reduced to 200 rpm and maintained for the subsequent 23 hours. It resulted in a clear casting solution with no air bubbles and enough viscosity to be cast. Membrane preparation was concluded by spreading each casting solution on a glass plate with a 250 µm Gardner knife and left to dry in air at 40-45 °C for 24 h inside a LBX Instruments air drying oven.

To produce the TPU-based symmetric dense membrane (casting solution TPU 10%-DMF/ACET 90%; 90%DMF-10%ACET ratio), 40.50 g of DMF was weighed in a 100 mL Erlenmeyer flask with a screw cap, followed by 4.50 g of ACET. A 40 mm triangular magnetic stirring bar was added, and the mixture was stirred at 600 rpm using a magnetic stirrer at room temperature. Next, 5 g of the

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Elastollan® 1170 A 10 000 TPU was gradually added to the flask under continuous stirring, after which the flask was sealed with the screw cap. After 1 hour, the stirring speed was reduced to 200 rpm and maintained for the subsequent 23 hours. After the 24 h stirring period, the casting solution was left still for 1 h to allow air bubbles to dissipate, resulting in a clear casting solution with no air bubbles and enough viscosity to be cast. Membrane preparation was concluded by spreading the casting solution on a glass plate with a 250 μm Gardner knife, leaving the casted solution exposed to air for 1 min and, following the phase inversion technique, placing the glass plate in a coagulation bath of deionized water at room temperature for 24 h. Water once again acts as a nonsolvent and exchanges with DMF. After this time, the glass plate was removed from the water, and the membrane was left to dry exposed to the atmosphere.

Figure 4 shows the obtained TPU-based membranes.

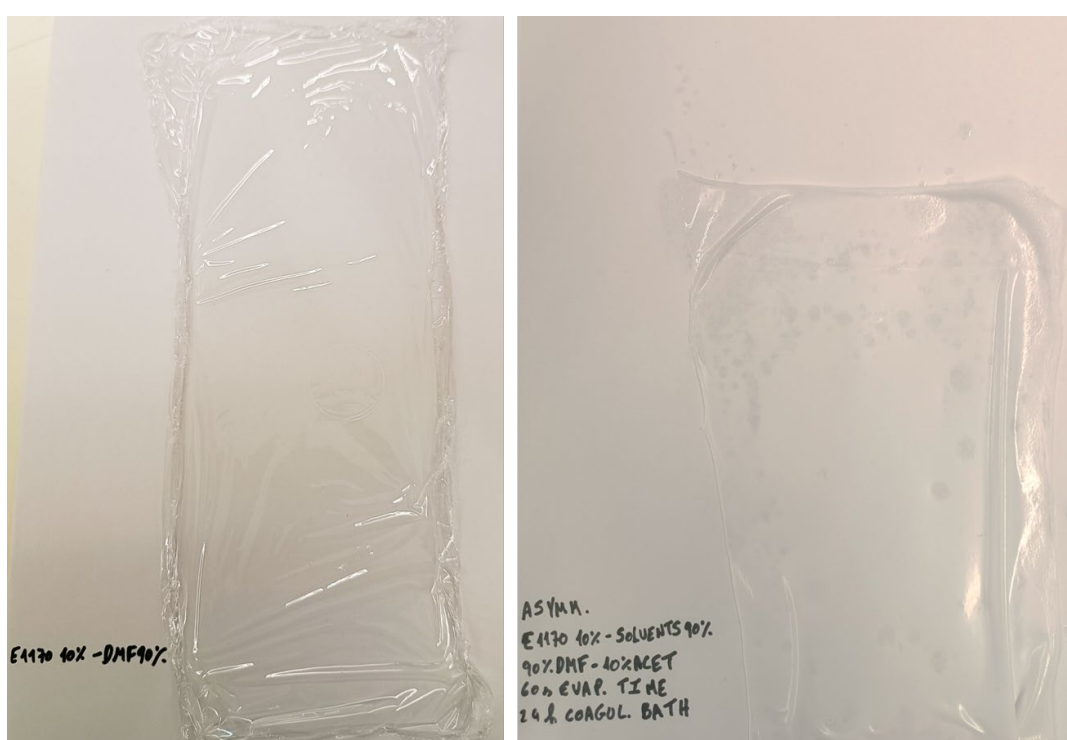


Figure 4: The obtained symmetric dense (left) and integrally asymmetric (right) Elastollan® 1170 A 10 000 TPU-based membranes.

5.5 Membrane characterization – Scanning Electron Microscopy (SEM)

PUR- and TPU-based membranes were characterized by SEM using a HITACHI S-2400 microscope (4 nm resolution at 25 kV). The samples were fractured after freezing in liquid nitrogen, mounted on a stub, and sputter-coated with Au/Pd. Images of the cross-sections of the membranes were obtained.

5.6 Gas permeation measurements by the constant volume method

The gas permeation properties of the membranes were determined by the constant volume method using the experimental setup schematized in Figure 5. This method consists of applying a constant pressure of gas on the feed side of the membrane and then following the gas flux through the

membrane by measuring the variation of pressure with time in a constant volume receiving chamber on the permeate side. The theory and calculations related to these gas permeation experiments can be found in a previous paper.¹ Assays were performed at 37.0 ± 0.2 °C considering transmembrane pressures (TMP) between 1 and 3 bar, with membranes being degassed between 15-20 h. The gas permeates through a 24.2 cm^2 membrane area while the variation of the permeate pressure into the receiving chamber (initially at vacuum state) is recorded as a function of time. Previous calibration of the unit allowed the determination of volumes of the permeate side (tubing volume of $13.7 \pm 0.1 \text{ cm}^3$; cylinder 1 volume of $12.6 \pm 0.1 \text{ cm}^3$; cylinder 2 volume of $167.3 \pm 0.1 \text{ cm}^3$).

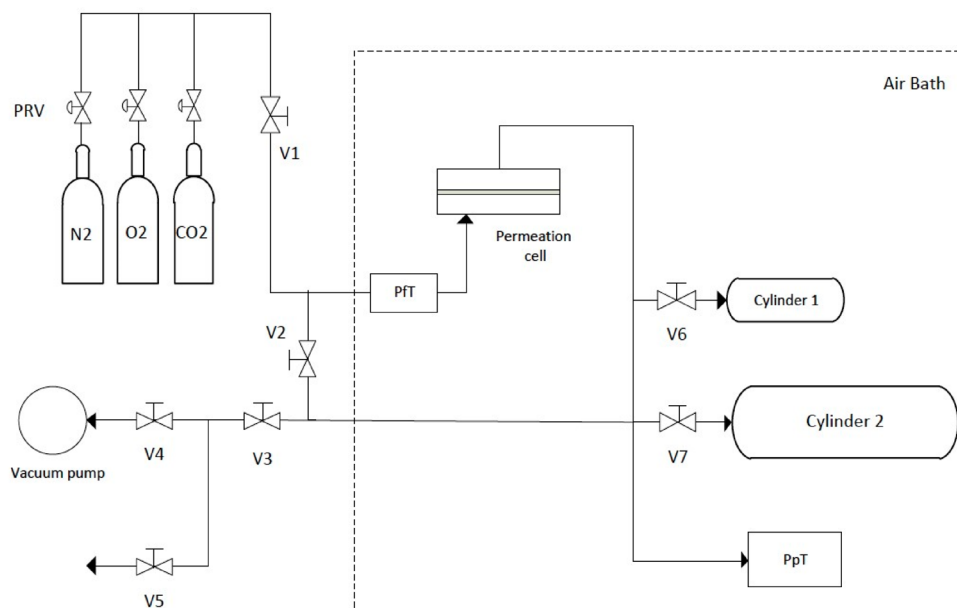


Figure 5: Schematic representation of the custom-built experimental gas permeation setup. V1–7: needle valves, PRV: pressure regulator valves, PFT: feed pressure manometer, PpT: permeate pressure manometer.

6 Results and Discussion

6.1 Membrane characterization – Scanning Electron Microscopy (SEM)

The micrographs of membranes shown in Figures 6 and 7 reveal that the symmetric dense PUR-, PUR/PCL-, and TPU-based membranes exhibit no visible pores in their cross-section. This was expected for this typology of membranes.

In contrast, the integrally asymmetric membranes display a distinct porous support layer beneath the very thin dense top layer. The support layer of the PUR- and PUR/PCL-based membranes has a sponge-like porous network, unlike the finger-like porous structure observed in the TPU-based asymmetric membrane.

¹ Eusébio et. al., "Sorption/Diffusion Contributions to the Gas Permeation Properties of Bi-Soft Segment Polyurethane/Polycaprolactone Membranes for Membrane Blood Oxygenators", *Membranes* 2020, 10, 8, DOI: 10.3390/membranes10010008.

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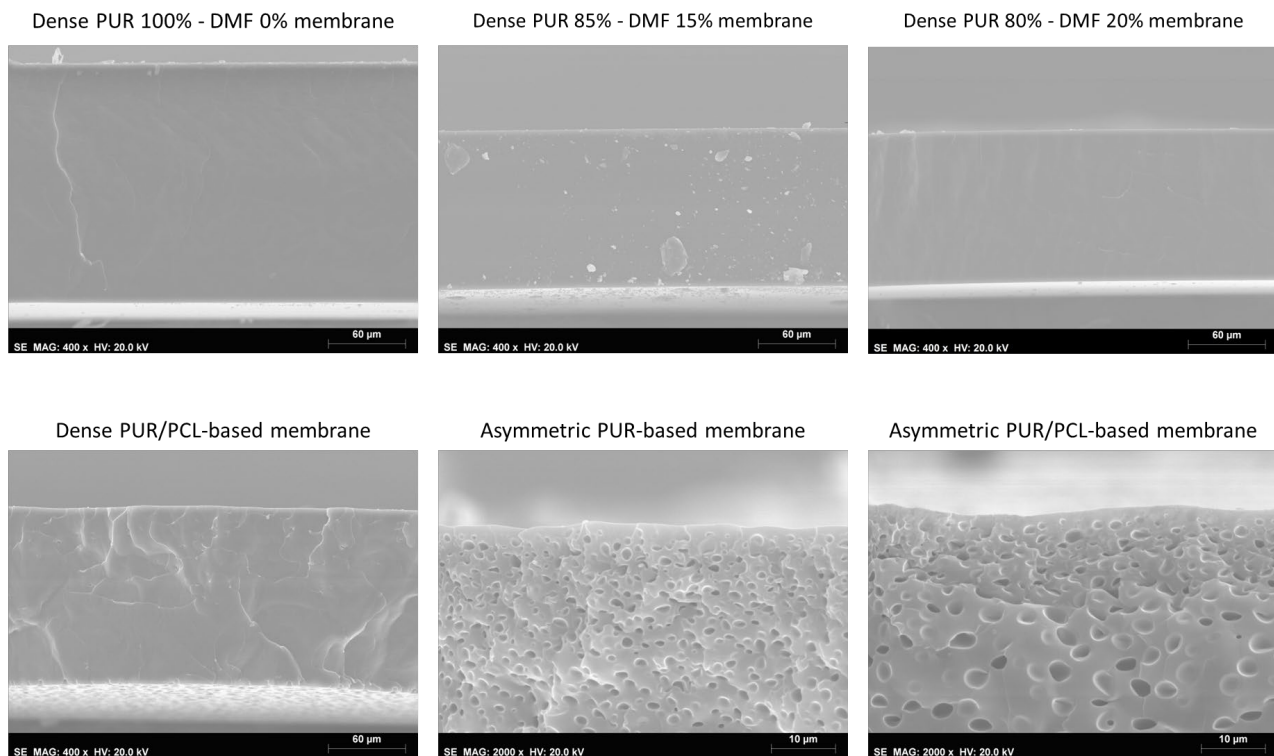


Figure 6: SEM micrographs of PUR- and PUR/PCL-based membranes (400x magnification for symmetric dense membranes; 2000x magnification for integrally asymmetric membranes).

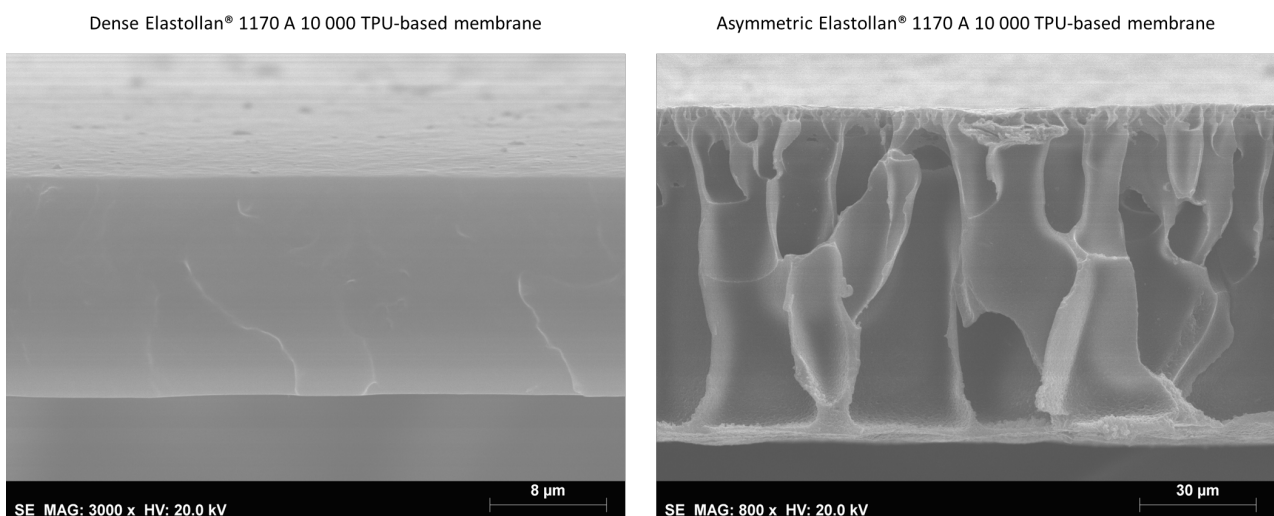


Figure 7: SEM micrographs of TPU-based membranes (3000x magnification for symmetric dense membrane; 800x magnification for integrally asymmetric membranes).

6.2 Gas permeation measurements by the constant volume method

The O₂ and CO₂ permeation performance of PUR-, PUR/PCL-, and TPU-based membranes was assessed and compared. Figure 8 illustrates O₂ and CO₂ permeation curves obtained during a single-gas permeation experiment using the symmetric dense PUR 80%-DMF 20% membrane. These results consistently show higher permeation rates for CO₂ compared to O₂, a trend observed across all membranes, regardless of composition or topology.

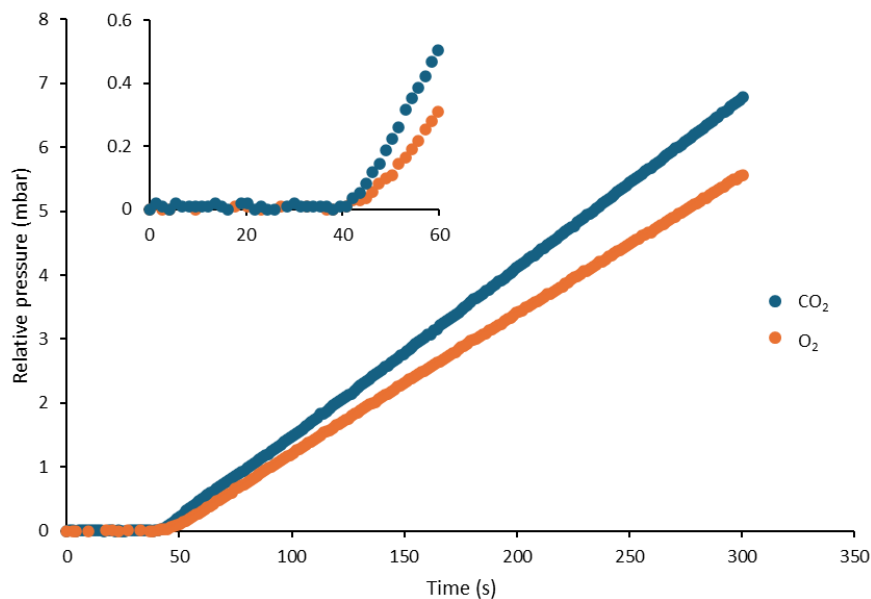


Figure 8: Permeate relative pressure as a function of time for O₂ (cylinder 2 closed) and CO₂ (experiments with both cylinders open) at a TMP of 3 bar. The inset highlights the low-permeation-time region (<60 s).

Permeation experiments conducted at various TMPs enabled the calculation of membrane permeance, determined from the linear relationship between gas flux and TMP. Figures 9 and 10 show the volumetric flux (*J*) of O₂ and CO₂ as a function of TMP for all membranes studied.

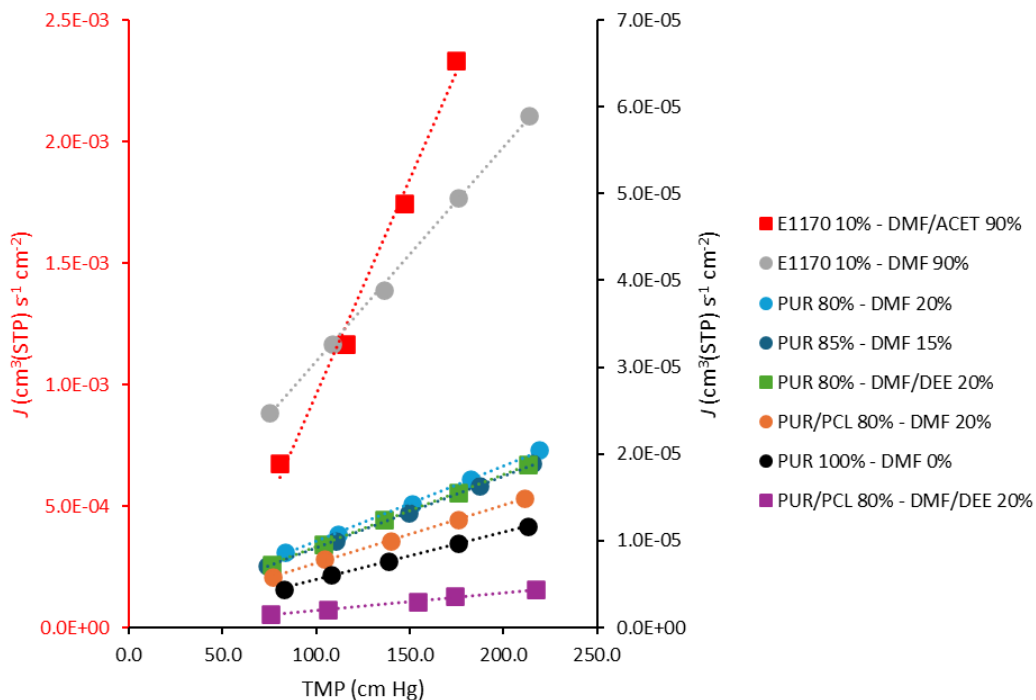


Figure 9: O₂ volumetric fluxes as a function of TMP for PUR-, PUR/PCL-, and TPU-based membranes. Symmetric dense membranes are represented by circles, and integrally asymmetric membranes by squares. Lines are fittings to the experimental points, highlighting the linearity of the collected data. The red y-axis applies only to the E1170 10% - DMF/ACET 90% membrane.

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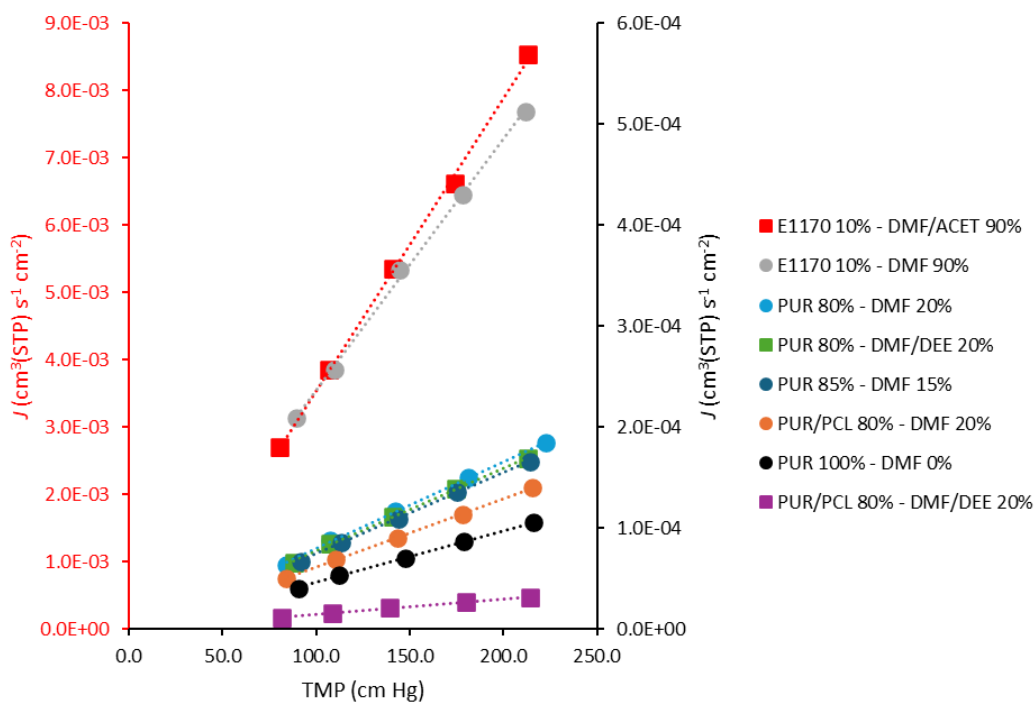


Figure 10: CO₂ volumetric fluxes as a function of TMP for PUR-, PUR/PCL-, and TPU-based membranes. Symmetric dense membranes are represented by circles, and integrally asymmetric membranes by squares. Lines are fittings to the experimental points, highlighting the linearity of the collected data. The red y-axis applies only to the E1170 10% - DMF/ACET 90% membrane.

Table 2 shows the results for the membranes prepared. The symmetric dense membranes can be compared in barrer units, as it is possible to determine with accuracy the thickness of the dense active layer. As the thickness of the active top layer is not so easy to determine in integrally asymmetric membranes, their results can be compared using gas permeance units, a characteristic of a membrane expressing the ability of a species to penetrate and permeate a membrane of a specific thickness.

The results in Table 2 reveal that the incorporation of PCL segments reduces gas permeance and permeability across all membrane types. Notably, the TPU-based membranes exhibit gas permeance values that are orders of magnitude higher than those of PUR- and PUR/PCL-based membranes. These findings emphasize the superior gas transport properties of TPU-based materials, suggesting their strong potential for further development. Future studies should prioritize the exploration of TPU-based membranes, leveraging the materials kindly provided by BASF SE to the IST group. Additionally, assessing their hemocompatibility is a critical next step.

Table 2: PUR-, PUR/PCL- and TPU-based membranes permeation performance. The abbreviation n.d. stands for “not determined”.

PUR-DMF casting solutions	Membrane thickness (μm)	O ₂ Permeance @ 37 °C ($\times 10^{-8} \text{ cm}^3 \text{ s}^{-1} \text{ cm}^{-2} \text{ cm Hg}^{-1}$)	O ₂ Permeability @ 37 °C (barrer)	CO ₂ Permeance @ 37 °C ($\times 10^{-8} \text{ cm}^3 \text{ s}^{-1} \text{ cm}^{-2} \text{ cm Hg}^{-1}$)	CO ₂ Permeability @ 37 °C (barrer)
PUR 100% - DMF 0%	185.9 \pm 0.5	5.5	10	51	95
PUR 85% - DMF 15%	122.7 \pm 0.4	8.3	10	80	98
PUR 80% - DMF 20%	117.9 \pm 0.3	8.7	10	86	101
PUR-DMF/DEE casting solution	Membrane thickness (μm)	O ₂ Permeance @ 37 °C ($\times 10^{-8} \text{ cm}^3 \text{ s}^{-1} \text{ cm}^{-2} \text{ cm Hg}^{-1}$)	O ₂ Permeability @ 37 °C (barrer)	CO ₂ Permeance @ 37 °C ($\times 10^{-8} \text{ cm}^3 \text{ s}^{-1} \text{ cm}^{-2} \text{ cm Hg}^{-1}$)	CO ₂ Permeability @ 37 °C (barrer)
PUR 80% - DMF/DEE 20%	n.d.	8.3	n.d.	82	n.d.
PUR/PCL-DMF casting solution	Membrane thickness (μm)	O ₂ Permeance @ 37 °C ($\times 10^{-8} \text{ cm}^3 \text{ s}^{-1} \text{ cm}^{-2} \text{ cm Hg}^{-1}$)	O ₂ Permeability @ 37 °C (barrer)	CO ₂ Permeance @ 37 °C ($\times 10^{-8} \text{ cm}^3 \text{ s}^{-1} \text{ cm}^{-2} \text{ cm Hg}^{-1}$)	CO ₂ Permeability @ 37 °C (barrer)
PUR/PCL 80% - DMF 20%	138.2 \pm 1.1	6.7	9	68	94
PUR/PCL-DMF/DEE casting solution	Membrane thickness (μm)	O ₂ Permeance @ 37 °C ($\times 10^{-8} \text{ cm}^3 \text{ s}^{-1} \text{ cm}^{-2} \text{ cm Hg}^{-1}$)	O ₂ Permeability @ 37 °C (barrer)	CO ₂ Permeance @ 37 °C ($\times 10^{-8} \text{ cm}^3 \text{ s}^{-1} \text{ cm}^{-2} \text{ cm Hg}^{-1}$)	CO ₂ Permeability @ 37 °C (barrer)
PUR/PCL 80% - DMF/DEE 20%	n.d.	2.1	n.d.	16	n.d.
E1170 - DMF casting solution	Membrane thickness (μm)	O ₂ Permeance @ 37 °C ($\times 10^{-7} \text{ cm}^3 \text{ s}^{-1} \text{ cm}^{-2} \text{ cm Hg}^{-1}$)	O ₂ Permeability @ 37 °C (barrer)	CO ₂ Permeance @ 37 °C ($\times 10^{-6} \text{ cm}^3 \text{ s}^{-1} \text{ cm}^{-2} \text{ cm Hg}^{-1}$)	CO ₂ Permeability @ 37 °C (barrer)
E1170 10% - DMF 90%	15.0 \pm 0.1	2.5	4	2.5	37
E1170 – DMF/ACET casting solution	Membrane thickness (μm)	O ₂ Permeance @ 37 °C ($\times 10^{-5} \text{ cm}^3 \text{ s}^{-1} \text{ cm}^{-2} \text{ cm Hg}^{-1}$)	O ₂ Permeability @ 37 °C (barrer)	CO ₂ Permeance @ 37 °C ($\times 10^{-5} \text{ cm}^3 \text{ s}^{-1} \text{ cm}^{-2} \text{ cm Hg}^{-1}$)	CO ₂ Permeability @ 37 °C (barrer)
E1170 10% - DMF/ACET 90%	n.d.	1.8	n.d.	4.3	n.d.

7 CONCLUSIONS

The developed protocols made possible the casting of both symmetric dense and integrally asymmetric PUR-, PUR/PCL-, and TPU-based membranes.

SEM micrographs revealed that all the produced symmetric dense membranes showed no visible pores in their cross-sections, as expected for this membrane typology. Integrally asymmetric membranes displayed distinct structural differences. While the PUR- and PUR/PCL-based ones showed a sponge-like porous support layer, the TPU-based one revealed a finger-like porous support layer.

Regarding their gas permeation performance, the incorporation of the PCL segment in bi-soft segment membranes resulted in a reduction in gas permeance/permeability, regardless of membrane topology. TPU-based membranes exhibited gas permeance values orders of magnitude higher than their PUR- and PUR/PCL-based counterparts, demonstrating their superior gas transport performance.

TPU-based materials provided by BASF showed remarkable promise for advanced membrane development. Future studies should prioritize optimizing these membranes for improved O₂ and CO₂ gas permeation targeting a novel generation of artificial respiration devices. This will be achieved by producing mixed matrix membranes (MMMs) using metal-organic frameworks (MOFs) as fillers. Additionally, a critical next step involves evaluating the hemocompatibility of TPU-based membranes to assess their suitability for the desired application.

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