DELIVERABLE

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D5.1 Nanoparticle Dispersion

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CONTENTS

1 EXECUTIVE SUMMARY

This document presents the deliverable D5.1 “Nanoparticle Dispersion” of the EIC Pathfinder Open project BioMembrOS. Herein, the protocols developed to produce symmetric dense and integrally asymmetric TPU-based membranes are presented. MOF nanoparticle dispersions were successfully achieved by creating homogeneous casting solutions to produce both symmetric dense and integrally asymmetric MMMs. This deliverable sets guidelines for producing TPU-based membranes that can be adapted should the TPU be changed, be it pure polymeric membranes or MMMs.

2 KEYWORD LIST

Artificial respiration
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
DCM	Dichloromethane
DMF	Dimethylformamide
EIC	European Innovation Council
IST	Instituto Superior Técnico
MMM	Mixed matrix membrane
MOF	Metal-organic framework
TPU	Thermoplastic polyurethane
UiO	Universitetet i Oslo

4 INTRODUCTION

In this document, the deliverable D5.1 “Nanoparticle Dispersion” for the EIC Pathfinder Open project BioMembrOS is presented. The nanoparticles considered herein are MOF ones dispersed in a TPU casting solution. This deliverable describes the methodology that was followed to obtain TPU casting solutions that allowed the production of membranes (both symmetric dense and integrally asymmetric ones) for gas permeation of the target gases (O_2 and CO_2). These membranes are to be used in a novel generation of artificial respiration devices (i.e., blood oxygenators). This document also reveals the methodology that was followed to produce casting solutions that have MOF nanoparticles included in their composition, leading to the production of MMMs. The inclusion of MOF nanoparticles within the polymeric matrix of the TPU is meant to increase the permeability to the target gases, with a particular focus on O_2.

The methodology contained in this deliverable is meant to be adaptable to the TPU that is used, even though a change in the casting solution composition will likely be required. Additionally, the described methodology to produce the MOF nanoparticle dispersion is also adaptable to the particle size of the MOF.

5 METHODOLOGY

5.1 Casting solution for symmetric dense membranes

The initial test to produce a casting solution started with mechanical stirring at room temperature of Elastollan® 685 A 10 000 (a polyester-based TPU), using a magnetic stirrer at 1000 rpm. For this, 5 g of Elastollan® 685 A 10 000 pellets were weighed and added to a round-bottom flask, and 1 g of DMF was added multiple times to the flask. At some point, the stir bar could not dissolve the TPU, as the pellets agglomerated to the bottom of the flask and formed a hardened layer. Manual dissolution was then performed using a glass rod; 27 g of DMF in total was enough to dissolve this TPU, but the viscosity of the solution was visually deemed as too low for its casting.

After this, it was decided that the dissolution of the TPU in DMF would be done using a wrist action shaker. Therefore, different amounts of DMF would be weighed first and then the TPU would be added secondly, followed by prompt shaking of the mixture. This would hinder the immediate aggregation of the TPU pellets. Different compositions were tested, always using 5 g of TPU and a content of DMF below 27 g. Table 1 shows the composition of different tested casting solutions, all of which were prepared in an Erlenmeyer flask with a screw cap, and shaken at room temperature for 48 h.

Table 1: Tested casting solution compositions for Elastollan® 685 A 10 000 to produce symmetric dense membranes.

Casting solution TPU%-DMF%	TPU (g)	TPU (wt.%)	DMF (g)	DMF (wt.%)
Casting solution 17-83	5.00	17.0	24.41	83.0
Casting solution 16.5-83.5	**5.00**	**16.5**	**25.30**	**83.5**
Casting solution 16-84	5.00	16.0	26.25	84.0
Casting solution 15-85	5.00	15.0	28.33	85.0

All the compositions 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 48 h. Given the visual viscosity of each casting solution, it was considered that the 16.5%TPU-83.5%DMF (found in Table 1 in bold letters) was the best one. Figure 1 shows the obtained membrane for this casting solution composition.

Figure 1: Symmetric dense membrane obtained from the 16.5%TPU-83.5%DMF casting solution.

5.2 Casting solution for integrally asymmetric membranes

To produce integrally asymmetric membranes, a pair of solvents need to be used to form the casting solution. The chosen solvents were DMF (boiling point of 153 °C and able to dissolve the Elastollan® 685 A 10 000 TPU) and acetone (boiling point of 56 °C, unable to dissolve the chosen TPU). It should be noted that acetone is considered a green solvent, and therefore was preferred over other solvents with low boiling points (e.g., diethyl ether). During the casting, the time-controlled evaporation of acetone at the membrane surface in contact with air will allow the formation of a very thin dense layer at the top of a porous support layer. Given that the thickness of the membrane dense layer is the main resistance to transport in gas permeation applications, the total flux for integrally asymmetric membranes is higher than that of symmetric dense membranes.

Table 2 shows the composition of the tested casting solution for an integrally asymmetric membrane. The DMF was weighed first into an Erlenmeyer flask with a screw cap, and then the TPU

was added, followed by prompt shaking of the mixture for 48 h. After this time, the Erlenmeyer was unscrewed to check if DMF had evaporated. As this was not verified, acetone was then added to the flask. The Erlenmeyer flask was then screwed and shaken again for 1 h.

Table 2: Casting solution composition for Elastollan® 685 A 10 000 to produce an integrally asymmetric membrane.

Casting solution TPU%-DMF%-ACET%	TPU (g)	TPU (wt.%)	DMF (g)	DMF (wt.%)	ACET (g)	ACET (%)
13.9-70.6-15.5	**5.00**	**13.9**	**25.30**	**70.6**	**5.54**	**15.5**

A clear casting solution with no air bubbles was obtained. 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. In this case, water 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 2 shows the obtained membrane for this casting solution composition.

Figure 2: Integrally asymmetric membrane obtained from the 13.9%TPU-70.6%DMF-15.5%ACET casting solution.

5.3 MOF nanoparticle dispersions

The casting solutions of MMMs were obtained by MOF dispersion in the TPU/solvent system mixture. The MOF UiO-66(Zr) was chosen to be dispersed in the previously-reported symmetric dense and integrally asymmetric membrane casting solutions because of its chemical and structural stabilities, even in the presence of biological fluids.

5.3.1 MOF synthesis

The synthesis of MOF UiO-66(Zr) first started by weighing 13.6095 g (81.9 mmol) of terephthalic acid ($C_6H_4(COOH)_2$, 166.13 g/mol, ≥98%, Thermo Scientific) and 26.3050 g (81.6 mmol) of zirconyl chloride octahydrate ($ZrOCl_2{\cdot}8H_2O$, 98%, Alfa Aesar) in separate beakers. The reagents were respectively dissolved in 35 and 160 mL of dimethylformamide (DMF, $HCON(CH_3)_2$, 73.09 g/mol,

≥99.9%, Carlo Erba). The content of each beaker was added to a reactor (Lab1st) already containing 250 mL of DMF, with a stirring rate of 80 rpm. The beaker containing the zirconyl chloride octahydrate was added first. After this, 27 mL of hydrochloric acid (HCl, 1M, Fisher Scientific) was added dropwise to the reactor. The stirring was changed to 170 rpm and the reaction took place under reflux at 383.15 K, using an oil bath (Lab1st) for 18 h. After this time, the reaction was stopped, and the content of the reactor was naturally cooled. Vacuum filtration was used to separate the MOF from the liquid phase. The MOF was placed in a cellulose extraction thimble and placed in a DMF bath at 343.15 K for 24 h to remove possible remaining unreacted/excess ligand. The extraction thimble was placed inside a Soxhlet extractor for successive extractions with dichloromethane (DCM, CH_2Cl_2, 84.93 g/mol, ≥99.8%, Sigma-Aldrich) for 24 h. The average extraction cycle was between 40-45 min. This procedure allowed the DMF to be exchanged with DCM and removed from the MOF structure. After the extraction period, the MOF was removed from the cellulose extraction thimble and dried at 393.15 K for 18 h inside a drying oven (LBX Instruments). Around 21 g of UiO-66(Zr) were obtained.

5.3.2 Casting solutions for MOF-dispersed MMMs

The composition of the casting solutions is shown in Table 3, where the MOF content made up for approximately 1 wt.% of the casting solution composition. The MOF was first dispersed in 3.8 g of DMF before this mixture was added to the Erlenmeyer flask that contained the TPU/solvent system mixture.

Table 3: Casting solution compositions for Elastollan® 685 A 10 000 to produce symmetric dense (top) and integrally asymmetric (bottom) membranes.

Casting solution TPU%-DMF%-MOF%	TPU (g)	TPU (wt.%)	DMF (g)	DMF (wt.%)	ACET (g)	ACET (%)	MOF (g)	MOF (%)
15.4-83.7-0.9	**10.00**	**15.4**	**54.40**	**83.7**	**-**	**-**	**0.61**	**0.9**
Casting solution TPU%-DMF%-ACET%-MOF%	**TPU (g)**	**TPU (wt.%)**	**DMF (g)**	**DMF (wt.%)**	**ACET (g)**	**ACET (%)**	**MOF (g)**	**MOF (wt.%)**
13.9-70.6-15.5	**10.00**	**13.1**	**54.40**	**71.4**	**11.08**	**14.5**	**0.73**	**1.0**

As previously mentioned, a dispersion of MOF in DMF was added to the TPU/solvent system mixture, which was then processed with an IKA T 10 basic ULTRA-TURRAX® equipment with a S 10 - 10 G - ST dispersion tool. It was observed in the first seconds that the casting solution changed colour and that, after 2 minutes of processing, the Erlenmeyer flask got hot and therefore it was decided to stop the dispersion of the MOF particles. Figure 3 shows the aspect of the nanoparticle dispersions.

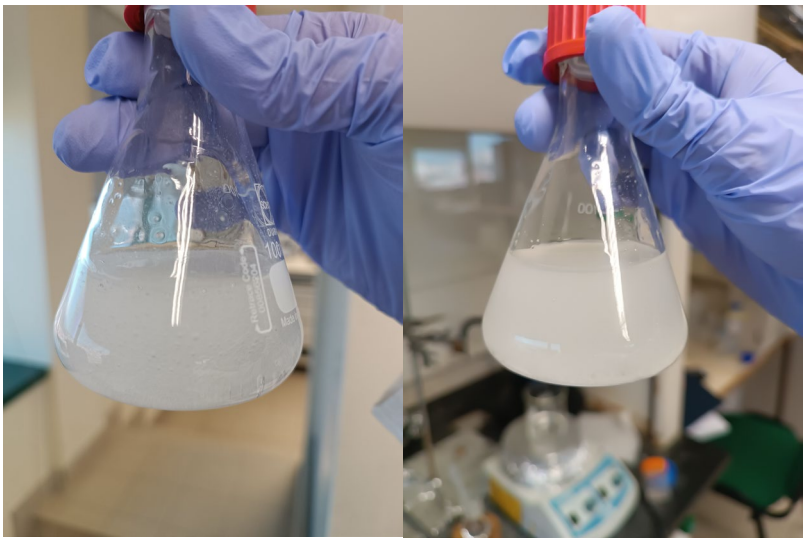

Figure 3: MOF nanoparticle dispersions to produce symmetric dense (left) and integrally asymmetric (right) MMMs.

The flask was then capped, and the solution was cast on a glass plate with a 250 µm Gardner knife. It was noted that air bubbles were still present in the nanoparticle dispersions, which afforded membranes with noticeable holes, as revealed in Figure 4. The nanoparticle dispersions were left still for 1 h so that the air bubbles dissipated; new membranes could be obtained with no noticeable holes, as shown in Figure 4.

Figure 4: (Left) Integrally asymmetric MMM obtained from the nanoparticle dispersion with air bubbles present; (Right) Integrally asymmetric MMM obtained from the nanoparticle dispersion with no air bubbles.

After membrane casting, the nanoparticle dispersions were capped and left still for 72 h. After this time, as seen in Figure 5, it was noticeable that there were still dispersed MOF nanoparticles. However, big MOF particles had sedimented to the bottom of the Erlenmeyer flask. This means that short times must be considered between the production of the MOF nanoparticle dispersion and the membrane casting.

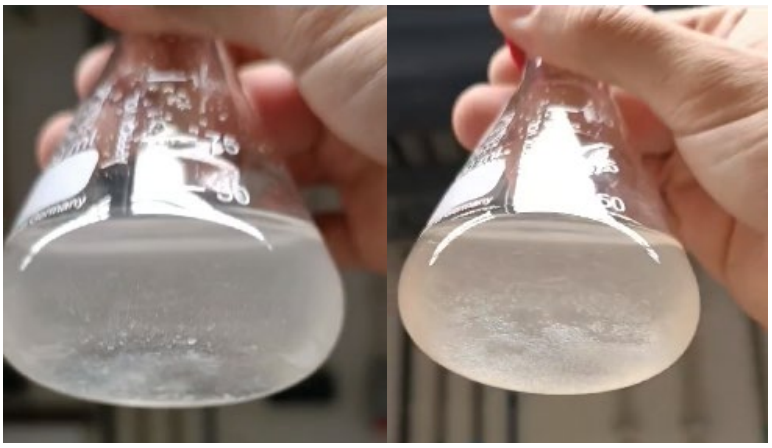

Figure 5: MOF nanoparticle dispersion for symmetric dense (left) and integrally asymmetric (right) MMMs after 72 h of being left still.

6 CONCLUSIONS

The developed protocols made possible the casting of both symmetric dense and integrally asymmetric membranes of the Elastollan® 685 A 10 000 TPU. With the IKA T 10 basic ULTRA-TURRAX® equipment with the S 10 - 10 G - ST dispersion tool, MOF nanoparticle dispersions were successfully obtained and can be used to produce both symmetric dense and integrally asymmetric MMMs.

7 LIST OF FIGURES

8 LIST OF TABLES