# MEMBRANES FORMATION BY SUPERCRITICAL FLUIDS

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**Abstract**

The generation of microporous cellulose acetate and polymethylmethacrylate (PMMA) membranes has been studied using a supercritical fluid based phase inversion process in which $CO_2$ acts as the non-solvent. Some experiments have been performed at 200 bar and 45°C with 20% w/w concentration of PMMA in dimethylsulfoxide (DMSO) and with concentrations ranging from 20 to 40% w/w of cellulose acetate in acetone. The structure of the resulting membranes has been analysed using scanning electron microscopy. We obtained membranes with a mean pore diameters ranging from 2 to 20 μm and a dense skin surface. Further experiments will be performed to investigate the effect of the other process parameters on these membranes morphology and pore sizes.

## 1. INTRODUCTION

Today the majority of porous membranes used in microfiltration, ultrafiltration and dialysis are prepared from an homogenous polymer solution by the wet phase inversion method [1-6]. A solution consisting of polymer and solvent is immersed into a non-solvent coagulation bath, where the contact between the solvent and the non-solvent causes the solution to be phase-separated. This process involves the use of organic solvents that must be expensively removed from the membrane with post-treatments, since residual solvents can cause potential problems for use, for example, in biomedical applications. Moreover, long formation times and a limited possibility to modulate cell size and membrane structure characterize this process.

Recently, Kho et al. [7] used a new technique in which supercritical $CO_2$ is used to induce the phase separation of the polymer solution. Compared with the wet phase inversion method, advantages of this phase separation process can be:

(1) Supercritical $CO_2$ can dry the polymer membrane rapidly. The dry membrane can be obtained without additional post-treatments.

(2) It is easy to recover the solvent; the solvent dissolved in supercritical $CO_2$ can be removed from gaseous $CO_2$ in a separator located downstream the membrane formation vessel.

(3) $CO_2$ is not toxic, not flammable and cheap.

Kho et al. [7] used compressed $CO_2$ for the formation of Nylon 6 membranes. Uniform structures with cellular pores of 0.4 μm in diameter were obtained. The authors concluded that reducing the relative strengths of both the solvent and the non-solvent, led to membrane pore

structures dominated by cristallization (S-L demixing), that is the thermodynamically favoured demixing process, rather than L-L demixing, which is kinetically favoured.

Another membrane formation process, in which supercritical $CO_2$ is used as the non solvent, has been presented by Matsuyama et al. [8-9]. This process consists of the introduction of $CO_2$ into a membrane formation cell through a buffer tank using a valve that connects the two vessels. After the system has been equilibrated (for 15 min) a second valve is opened and $CO_2$ flows in the cell to dry the phase-separated polymer solution. Matsuyama et al. [8] studied the formation of polystyrene membranes analysing the effect of several process conditions (temperature, pressure, polymer concentration). The average pore size ranged from 8 to 35 μm changing pressure (from 75 to 150 bar), polymer concentration (from 15 to 30% w/w) and temperature (from 20 to 70°C).

In a subsequent work, Matsuyama et al. [9] studied the influence of different solvents during the formation of cellulose acetate membranes. The authors worked with fixed process parameters: pressure, temperature and polymer concentration (130 bar, 35°C, 15% w/w) and tested four solvents: acetone, methyl acetate, 1,3-dioxolane and 2-butanone. The results showed that as the mutual affinity between the solvent and $CO_2$ decreases, the membrane porosity and the pores size increases.

In conclusion, the $CO_2$ assisted process for producing membranes seems to be very promising. Until now, only few polymers have been tested and a limited analysis of the effect of the process conditions has been performed. Therefore, in this work we used a supercritical fluid assisted phase inversion method (SAPIM) to study the formation of cellulose acetate and PMMA membranes. We also studied the effect of polymer concentration on cellulose acetate membranes morphology. An attempt to explain the process evolution has been performed.

## 2. EXPERIMENTAL SECTION

### *2.1 Materials*

Cellulose acetate, polymethylmethacrylate (PMMA), dimethylsulfoxide and acetone were bought from Sigma-Aldrich; $CO_2$ (purity 99%) was purchased from S.O.N. (Società Ossigeno Napoli, Italy). All materials were processed as received.

### *2.2 Apparatus and Methods*

The membranes were prepared in a home-made laboratory apparatus equipped with a 316 stainless steel cylindrical high-pressure vessel with an internal volume of 200 mL, in which $CO_2$ contacts the sample in a single pass bed. The vessel is immersed in a thermostated oven. The polymer solution is placed in a membrane formation cell inside the vessel that is then heated and filled with supercritical $CO_2$ up to the desired pressure using a high pressure pump (Milton Roy – Milroyal B). In the first part of the process, $CO_2$ penetrates in the solution operating in batch mode for 1h; after this period of time, a micrometric valve is opened and continuous mode was obtained; i.e., a constant $CO_2$ flow of 1.2 Kg/h was used, holding pressure and temperature constant to dry the phase-separated membrane for 2h. Then, the vessel was slowly depressurised for 2h. Thin membranes with thicknesses ranging from 100 to 700 μm and diameter of about 2.5 cm were obtained.

*2.3 Membranes Characterization*

Cellulose acetate and PMMA membranes were characterized to determine cell size and structure. The cellular structure was examined by cryofracturing the membrane using a microtome (Bio-optica S.p.A – mod Microm HM 550 OMVP), sputter-coating it and viewing it by SEM (mod. LEO 420). Sigma Scan Pro software (Jandel scientific version 5.0) and Origin 5 (Microcal) software were used to measure the average value of the pores and to calculate cell diameter distributions.

## 3. RESULTS AND DISCUSSION

*3.1 PMMA membranes*

In the first part of the work, we processed a polymer solution formed by PMMA and DMSO, containing a percentage of 20% w/w of polymer, in a set of experiments performed at 45°C and 200 bar. In **Figure 1** an example of the PMMA membranes is reported.

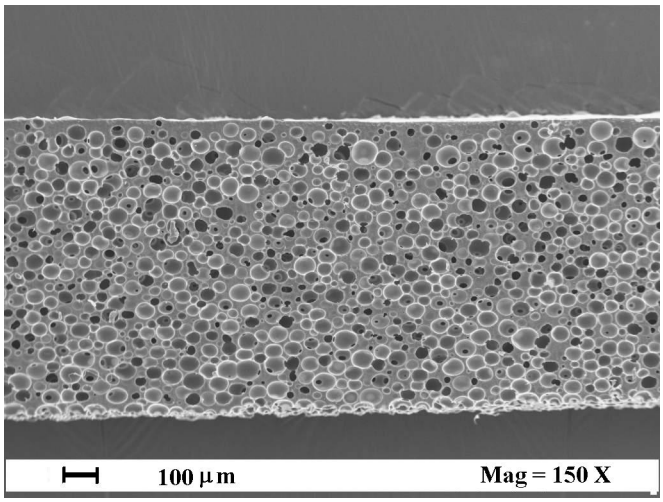



**Figure 1: PMMA membrane section operating at 200 bar, 45°C and 20% w/w**

At this operating conditions a continuous surface has also been obtained, whereas the internal of membrane presents a regular porous structure with a cellular morphology (**Figure 2)**. The mean diameter of pores is about 20 µm.

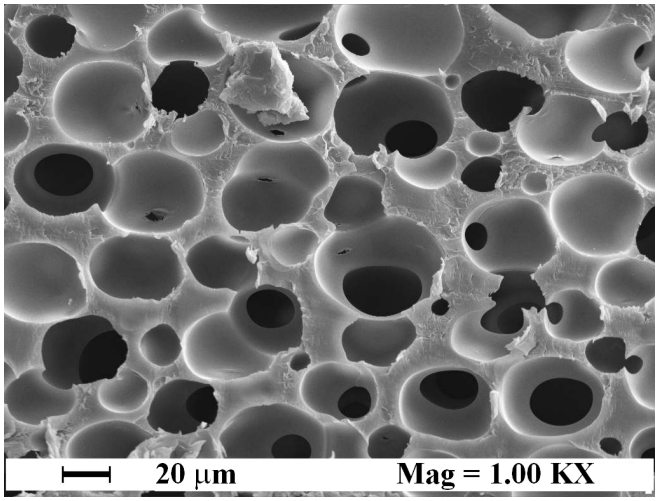
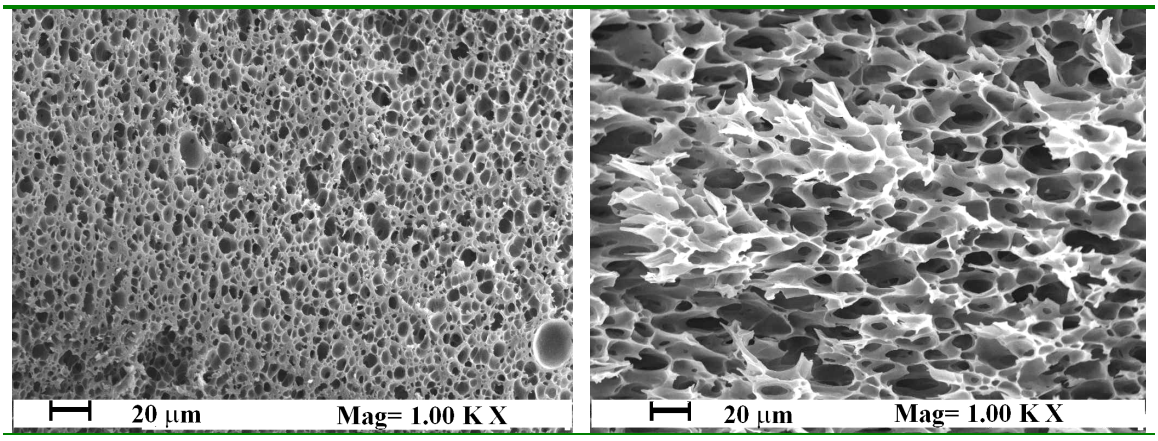



**Figure 2: PMMA membrane section operating at 200 bar, 45°C and 20% w/w**

*3.2 Cellulose Acetate membranes*

We processed some cellulose acetate solutions containing percentages of polymer from 20 to 40% w/w in acetone, in a set of experiments performed at 45°C and 200 bar. Examples of membrane sections are shown in **Figure 3**. It is evident the increase of pore size with the decrease of cellulose acetate concentration.




**a)** **b)**

**Figure 3: Cellulose acetate membrane sections operating at 200 bar, 45°C, (a) 40% w/w, (b) 20% w/w.**

At these operating conditions a continuous surface has been obtained only for solutions with over 30% w/w of polymer. Pore size distributions at different polymer concentrations are shown in **Figure 4** that confirms the qualitative information given by **Figures 3a, 3b.** Increasing the amount of polymer from 20 to 40 % w/w the mean diameter of the cells decreases from 10 μm to 2 μm and the pore size distribution sharpens. All distributions are quasi symmetric.

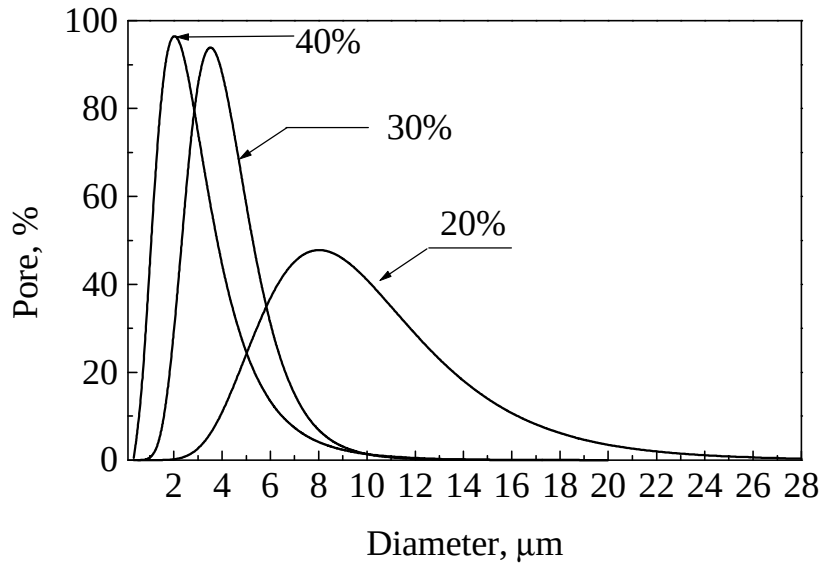



**Figure 4: Cellulose acetate membranes pore size distribution at different polymer concentration operating at 45°C and 200 bar.**

A proposed mechanism of membranes formation using the classic phase inversion method with two organic solvents [1] indicates that the phase separation process responsible of the porous cellular structure can be the L-L demixing by nucleation and growth of the polymer from the lean phase. The subsequent removal of the solvent produces a dry and stable structure. The role of S-L demixing process on the membrane morphology has been also studied [10]. Depending on the solvent and non-solvent combination used, membranes could be obtained with either a structure largely due to L-L demixing (cellular morphology) or with a structure due to S-L demixing (leafy morphology).

In the case of SAPIM, we obtained PMMA and cellulose acetate membranes with a cellular morphology. This results indicate that, probably, a L-L demixing mechanism similar to that described by Van de Witte et al. [1] for classical phase inversion method is the process controlling the formation of these membranes.

Moreover, we observed that increasing the cellulose acetate concentration, the pore size decreases, due to an increase of the viscosity of the sample. As a consequence, a slower demixing is obtained and the polymer can rearrange to form a structure with smaller pores. Also in this case a similar result is observed for classical L-L demixing process [1].

In conclusion, the supercritical fluid based process produces membranes rapidly and without any post-treatment. Moreover, the large versatility of the supercritical fluid allows to modulate the pore size by simply changing the operative conditions.

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