

# MEMBRANE FORMATION WITH CO<sub>2</sub>-ASSISTED PHASE INVERSION METHOD. SOLVENT POWER AND DEPRESSURIZATION EFFECT.

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## ABSTRACT

In the present work polysulfone membrane were prepared using a CO<sub>2</sub>-assisted phase inversion method. N-Methylpyrrolidone, N,N-Dimethylacetamide and N,N-Dimethylformamide were used to solubilise the polymer. Preliminary results suggest that mutual affinity between solvent - CO<sub>2</sub> and depressurization are able to modulate the pore size and the surface of the membranes.

The experiments were undertaken at 318.15 K and at pressures up to 19.3 MPa.

## INTRODUCTION

A number of different techniques are available to prepare porous polymeric films, such as sintering, stretching, track etching, phase separation, sol-gel process, vapour deposition and solution coating [1]. However, the majority of porous flat membranes are prepared from a homogenous polymer solution by the wet-phase inversion method in which a polymer solution (polymer plus solvent) is cast on a suitable support and immersed in a coagulation bath containing a nonsolvent. Precipitation occurs due to the exchange of solvent and non-solvent. The membrane structure is the result of the combination of the mass transfer and phase separation.

Recently, supercritical carbon dioxide has been applied to induce the phase separation of the polymer solution and produce membranes of nylon [2], polystyrene [3], cellulose acetate [4], polysulfone [5] and polylactide [6].

There are several reasons to continue the implementation of supercritical fluids (SCF), especially carbon dioxide, as alternative solvents for the synthesis and processing of porous materials [7]:

- Environmentally friendly and readily available in high purity.
- Capacity to produce homogeneous membranes.
- Recovery of a dry polymeric product – most SCF solvents are gases under ambient conditions.
- Relatively easy to recover the solvent.
- Additional parameters (pressure, temperature, depressurization) to improve the morphology of the membrane.

- Improvement in the mass transfer – SCF solvents have much lower viscosities, than organic liquids, which can be easily adjusted with variations in pressure and temperature.

The main goal of this work was the analysis of the solvent affinity and depressurization rate influence in the morphology of polysulfone membranes. Polysulfone is one of the classic polymers used for membrane preparation and also an important material in the field of polymeric membranes because of its mechanical, thermal and chemical stability as well as its excellent film forming properties [8].

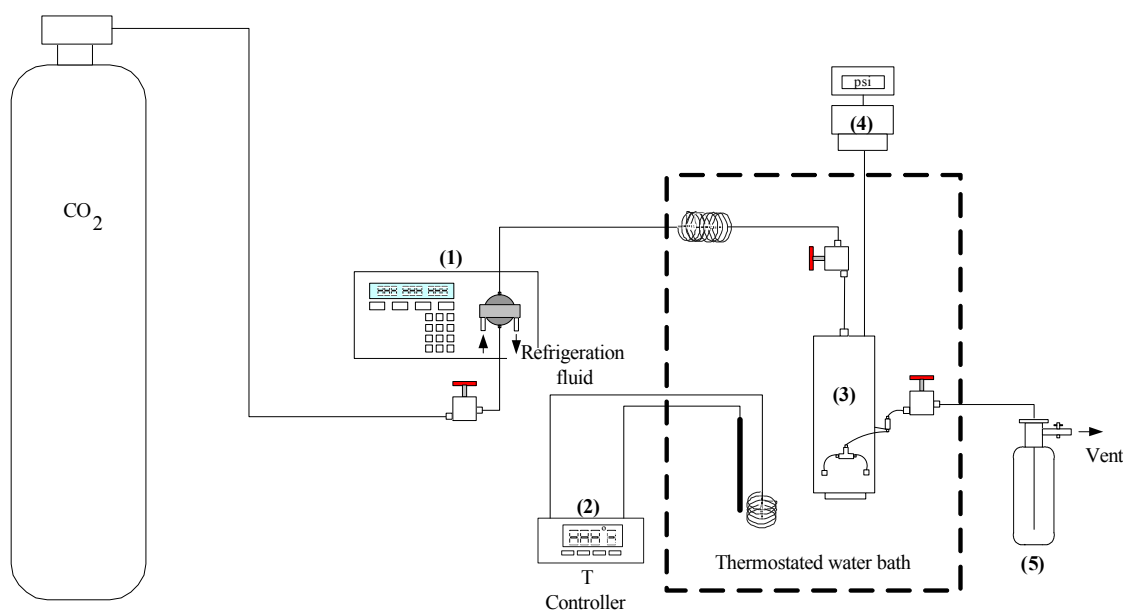
## EXPERIMENTAL SECTION

### Materials.

Polysulfone (molecular weight 67,000) was obtained from Sigma-Aldrich in pellet form. The solvents N-Methylpyrrolidone (purity  $\geq 99.5\%$ ) and N, N-Dimethylacetamide (purity  $\geq 98\%$ ) were purchased from Sigma-Aldrich and N,N-Dimethylformamide (purity  $\geq 95\%$ ) from May & Baker. Carbon dioxide was obtained from Air Liquide with 99.998% purity. All reagents were used without any further purification.

### Methods.

Polymer solutions were prepared in order to obtain a 15% wt solution. To promote the phase inversion a new high pressure apparatus, schematically presented in Figure 1, was designed.



**Figure 1.** Schematic diagram of the apparatus: (1) Gilson 305 Piston Pump; (2) Temperature controller; (3) High-pressure cell; (4) Pressure transducer (5) Trap

This apparatus was built around a 33 ml cylindrical cell with an interior mechanism to homogeneously disperse CO<sub>2</sub> in the top of the solution. In the bottom, where the polymer solution is placed, it has one sapphire window sealed with a Teflon o-ring, and in the top a stainless steel screw-tap provides the mean to connect the CO<sub>2</sub> entrance and the pressure transducer. The cell is immersed in a visual thermostated water bath, heated by means of a controller (Hart Scientific, Model 2200) that maintained the temperature within  $\pm 0.01\text{ }^{\circ}\text{C}$ .

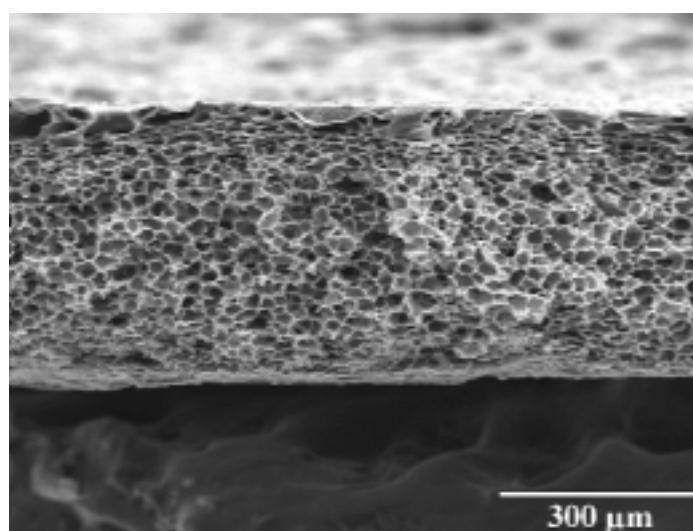
In a typical procedure, the polymer solution (approximately 400 mg) is loaded into the high-pressure vessel which is then placed in the thermostated water bath. CO<sub>2</sub> is added until the desired pressure, with the exact flow, using a Gilson 305 Piston Pump. After reaching it, the valve in the bottom of the cell is opened, to operate in continuous mode. All the experiments were realized at  $18.6 \pm 0.7$  MPa with a CO<sub>2</sub> flow of 9.8 g/min during 2 hours. To analyze the effect of depressurization, the vessel was depressurized at two different rates: in one hour and in less than one minute.

Membranes were characterized by optic microscopy and Scanning Electron Microscopy (SEM). They were prepared for SEM analysis by cryofracturing and were coated with gold.

## RESULTS AND DISCUSSION

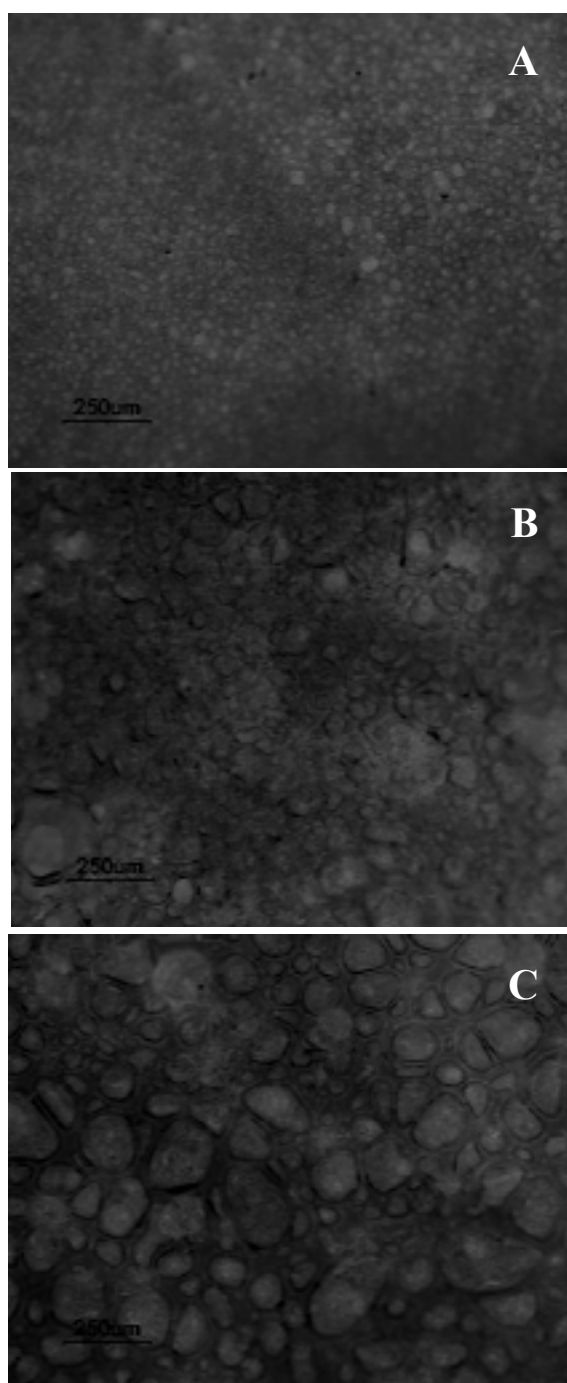
The preparation of porous polysulfone membranes using the supercritical CO<sub>2</sub> – assisted phase inversion method as already been reported in literature by Reverchon and Cardea [5]. They studied various polymer concentrations, temperatures and pressures conditions to produce homogeneous membranes with different pore size.

In this work we were also able to produce homogeneous membranes as demonstrated by the regular structures shown on figure 2.



**Figure 2.** SEM micrograph of the Cross Section structure of a polysulfone membrane (15.27 % w/w DMA, 45°C; 19.3 MPa, depressurization: 1 hour)

In this type of technique, the selection of the pair solvent-nonsolvent is very important to obtain the desired structural elements that form the porous structure.

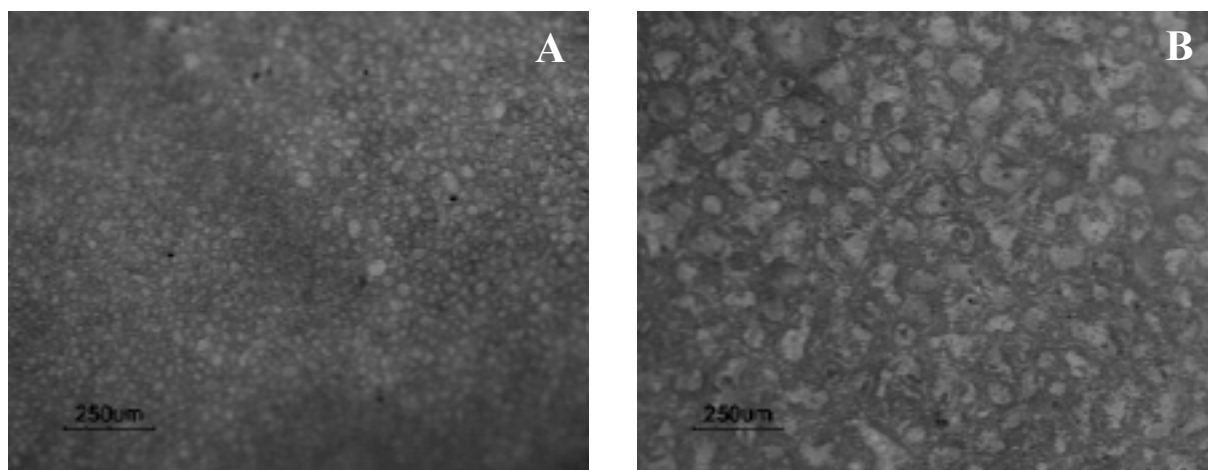


**Figure 3.** Solvent power effect in the Membrane Surface (captured with the optic microscope)  
A- NMP, B- DMA, C- DMF

Usual solvents for dissolving polysulfone are N-Methylpyrrolidone (NMP), N,N - Dimethylacetamide (DMA), N,N-Dimethylformamide (DMF) which are all aprotic and polar.

Furthermore, they are soluble in carbon dioxide [9] [10] [11], which is a nonsolvent for polysulfone.

Figure 3 shows the surface of three different membranes obtained in the same conditions with the exception of the solvent used. The differences observed are related with the mutual affinity between solvent and CO<sub>2</sub>. This same behavior has already been reported in literature by Matsuyama and co-workers [12] who tested four different solvents in the production of cellulose acetate membranes.



**Figure 4.** Depressurization rate effect in the membrane surface (captured with the optic microscope). Solvent: NMP, Temperature: 45°C; 17.9 MPa, A – depressurization in one hour, B – depressurization in less than one minute)

Another consideration explored in this work was the depressurization rate. Preliminary results suggest that the depressurization rate effect is mainly evidenced in the surface of the membrane (figure 4). Mainly because this is the region that presents higher fragility, in the structure, and so it is easier to collapse.

To better characterize the achieved structures the size distributions of the porous is being performed and will be presented in future work.

#### **ACKNOWLEDGEMENTS**

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