Characterization of Polysulfone Membranes Prepared with Thermally Induced Phase Separation Technique

L G Tiron*, Ș C Pintilie, M Vlad, I G Birsan and Ș Baltă
“Dunarea de Jos” University of Galati, str. Domnească nr. 111, 800201, Galați, Romania
E-mail: geanina.tiron@ugal.ro

Abstract. Membrane technology is one of the most used water treatment technology because of its high removal efficiency and cost effectiveness. Preparation techniques for polymer membranes show an important aspect of membrane properties. Generally, polysulfone (PSf) and polyethersulfone (PES) are used for the preparation of ultrafiltration (UF) membranes. Polysulfone (PSf) membranes have been widely used for separation and purification of different solutions because of their excellent chemical and thermal stability. Polymeric membranes were obtained by phase inversion method. The polymer solution introduced in the nonsolvent bath (distilled water) initiate the evaporation of the solvent from the solution, this phenomenon has a strong influence on the transport properties. The effect of the coagulation bath temperature on the membrane properties is of interest for this study. Membranes are characterized by pure water flux, permeability, porosity and retention of methylene blue. The low temperature of coagulation bath improve the membrane’s rejection and its influence was most notable.

1. Introduction
Technologies based on membrane separation are often applied in several industries: food, medicine, pharmacy and wastewater treatment [1]. The membrane can be fabricated from organic or inorganic materials. Nowadays, the most studied membrane materials are polymers because of their properties (mechanical, chemical and flexibility).

Polysulfone is an organic polymer widely used due to the chemical and thermal stability provided to the membrane [2].

Polymeric membranes can be obtained by applying phase separation process. There are two techniques according to the driving force to use phase separation: non-solvent induced phase separation (NIPS) and thermally induced phase separation (TIPS). To obtain membranes used in microfiltration, ultrafiltration, nanofiltration and reverse osmosis, the non-solvent induced phase separation (NIPS) is most used [3].

By this method, the thin film is immersed into the coagulation bath and the solvent from the casting solution is replaced by the nonsolvent (pure water) and phase inversion takes place. This technique is used to obtain asymmetric membranes [4–7].

Obtaining membranes with the phase inversion technique, their properties can be influenced by same parameters like: the polymer and solvent type and their concentration, casting solution temperature, the nonsolvent bath coagulation properties (temperature and composition), evaporation conditions and the process variables (casting speed) [8].

In this study, the polymer used is polysulfone (PSf) because of its chemical and mechanical
properties and is one of the most used material in ultrafiltration process [9]. Although the membranes obtained from PSf are restricted due to its hydrophobic properties [10], [11], resulting in a low water flux and serious membrane fouling [12].

A thermally induced phase separation (TIPS) technique is a method for preparing membranes which was implemented in the 1980s. Membranes prepared by the TIPS method usually have high strength and flux [13], [14].

Temperature reduction and double diffusion between solvent and water would occur at the same time by using water soluble solvents to prepare the membrane when the incipient membrane is immersed in a water coagulation bath. At the same time, a denser skin layer forms during the membrane formation process. Pores from membrane surface skin layer prevent activated sludge and other granular substances from entering inside the membrane pores. The antifouling property of membrane is improved [15].

2. Materials and methods

The support layer (Viledon FO2471) used for manufacturing the membrane was obtained from Freudenberg (Winheim, Germany). The membrane was obtained from polysulfone (PSf) polymer. The solvent used was 1-methyl-2-pyrrolidone (NMP, 99%). Both were purchased from Sigma-Aldrich.

The membranes were obtained using the immersion precipitation method, by phase inversion. The casting solution was prepared by adding the polysulfone polymer of 23 weight percentage in the NMP solvent under continuous stirring at 1200 rotations per minute for 24 hours.

The obtained solution was cast on the support layer (non-woven polyester). The support layer was wetted with the solvent to prevent the polymer solution from blocking the pores of the support layer. The homogeneous solutions were cast with 250 µm thickness on the support layer using a film applicator (Automatic Film Applicator PA-2101, BYC-Gardner GmbH). The casting film was immersed into the coagulation bath and kept in the bath for 30 min. The temperature of the coagulation bath has been set at 5, 20 and 40°C.

The polymer concentrations and the coagulation bath temperatures used to obtain the membranes are shown in Table 1.

| Membrane no. | PSf concentration \([\text{wt}\%]\) | Coagulation bath temperature \([\degree\,\text{C}]\) |
|--------------|---------------------------------|---------------------------------|
| PSf-1        | 23                              | 5                               |
| PSf-2        | 23                              | 20                              |
| PSf-3        | 23                              | 40                              |

2.1. Pure water flux

The membrane obtained were characterized by flux experiments with pure water in a dead-end filtration cell (Sterlitech HP4750 Stirred Cell) at an operating pressure of 10 bar using an inert gas (nitrogen) at room temperature (approx. 25°C). The pure water flux \( J_w \) was calculated as follows

\[
J_w = \frac{V}{A \cdot t} \Rightarrow J_w = \frac{V}{A \cdot t}
\]  

Where \( V \) is the volume of permeate collected during the time interval \( t \) through an effective membrane area \( A \). The permeability tests were performed at four different pressures 6, 8, 10 and 12 bar.

The pure water permeability \( (L/m^2 \cdot h \cdot \text{bar}) \) was calculated using the following expression:

\[
\text{Pure water permeability} = \frac{\text{Pure water flux}}{\Delta p}
\]  

Where \( \Delta p \) is the operating pressure (bar).
2.2. Retention tests
The retention of solids from a solution is the quantity of sludge that remains on the surface of the membrane through which the feed solution flows. In this study, it was observed the retention properties of the membrane samples with Methylene Blue dye with a molecular mass of 319.85 g·mol$^{-1}$. The dye concentration is determined spectroscopically using a UV-Vis Spectrophotometer HACH DR 5000 (Hach Lange GmbH, Germany).

The rejection ratio was calculated by the following equation:

\[
Retention [\%] = \left(1 - \frac{C_f}{C_0}\right) \times 100
\]  
(3)

Where $C_0$ represents dye concentrations in feed solution (100 ppm) and $C_f$ is the permeate concentration.

2.3. Hydrophilicity
The water affinity of the membranes was determined using contact angle measurements. The surface hydrophilicity of the prepared PSf samples was evaluated by using a contact angle goniometer (OCA 15EC, DataPhysics) to measure the contact angle between the polymer surface and water droplet.

Before contact angle measurements, membrane samples were dried at 5°C for 24 hours and stored in a vacuum desiccator. The dropping was repeated for several times for each sample.

2.4. Porosity
Porosity of a membrane has a very important role in permeability and retention. The porosity of the membrane is determined by the equation:

\[
Porosity = \frac{W_w - W_d}{\rho_w \times V}
\]  
(4)

Where $\rho_w$ is pure water density at room temperature (kg/m$^3$) and $V$ is membrane volume in wet case (m$^3$). $W_w$ and $W_d$ are the masses of a membrane, in wetted and dry state.

3. Results and discussions
In figure 1 it was observed that the flux of a membrane depends on the temperature of the coagulation bath. Increasing the temperature of the coagulation bath at 40°C leads to an increase in water flux.

![Figure 1](image-url)

Figure 1. Comparative flux Figure.
According to the Brownian motion, in a liquid-liquid system, the irregular motion of the molecules from the two liquids is directly proportional to temperature. Temperature increase will create a more chaotic movement of molecules [16]. In the phase inversion method, temperature is of great interest in the coagulation bath. Higher temperature of the coagulation bath will lead to a faster withdraw of the solvent from the polymer solution, creating larger and irregular pores, approved by the flux of PSf-3 membrane in figure 1. In the same time, lower temperatures will make the solvent exit the polymer solution in a more controlled manner, producing smaller pores, as show in figure 1 and 2.

The rejection of methylene blue with 100 ppm concentration was investigated for prepared membranes by measuring the retention flux as it can be seen in figure 2.

Figure 2 shows that the flux of PSf-3 membrane, obtained at 40°C, has a high decline comparative with the other two. When the coagulation bath temperature is low, the retention flux of membranes is more stable.

![Figure 2. Comparative retention flux.](image)

When analysing the average flux values, both in pure water and dye, PSf-1 has the lowest and unstable pure water flux. When we put the PSf-1 membrane in retention tests, we notice that the dye flux is higher than the membrane made at room temperature (PSf-2).

The retention coefficient tested is showed in figure 3. There is a tendency to increase the separation effect with decreasing the coagulation bath temperature. The permeability of the membrane is inversely proportional with the retention of methylene blue. The maximum performance of membrane retention is obtained at 5°C temperature of coagulation bath.

![Figure 3. Methylene blue retention and the permeability of the membranes.](image)
Water flux of the membrane obtained in coagulation bath with 40°C (PSf-3) is higher than water flux of the membrane obtained in coagulation bath with 5°C (PSf-1) due to the improvement of membrane hydrophilicity.

As can be seen in figure 4, the contact angle decreases as the coagulation bath temperature increases, meaning that the membrane surface is more hydrophilic and the porosity is higher.

![Figure 4. Hydrophilicity and porosity.](image)

Membrane porosity is higher by increasing the coagulation temperature because the heat transmission rate decreased. Increasing the porosity leads to the increase of pure water flux and the decrease of rejection process, also have an impact on the decrease of the membrane resistance.

4. Conclusions
The properties of the membrane are significantly influenced by the coagulation bath temperatures. As observed, the pure water flux increase when the coagulation temperature rises from 5°C to 40°C, but the retention decreases. The increasing temperature has also an impact on the increase of porosity because the solvent and the water diffusion is accelerated and forms a large pore volume. On the formation process of the thin layer, the higher temperature increases the dissolving rate of the polymer (PSf).

At 40°C of coagulation bath, membrane properties are improved, less retention of the methylene blue. The membranes obtained at low temperatures have a good stability and retention.

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