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Effect of different additives on the fabrication of hydrophilic polysulfone ultrafiltration membranes

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Polysulfone ultrafiltration membranes have been widely applied, especially for water and wastewater treatment. Polysulfone as membrane material presents several advantages, such as good mechanical properties, high thermal and chemical resistance, processing easiness, and wide availability in the market. However, the hydrophobic nature of the polysulfone membrane leads to a low water flux and increases the proneness to organic fouling. In order to overcome this problem, the effect of different additives and polymer concentration on the performance and morphology of polysulfone flat sheet membranes, prepared by phase inversion process, were investigated in this work. Several experimental sets were performed. The effect of polyvinylpyrrolidone to increase the pore density and membrane permeability was confirmed. Moreover, the effect of lithium chloride to reduce the amount of macrovoids in the membrane and to increase the viscosity of the casting solution was also confirmed. The fabricated membranes were characterized by atomic force microscopy, scanning electron microscopy, and infrared spectroscopy (ATR-IR). Furthermore, water permeability, retention tests to evaluate the molecular weight cut-off, and the real thickness of the prepared membranes as well as viscosity of the casting solutions were measured.

Keywords: Additive; Lithium chloride; Membrane preparation; Phase inversion; Polymeric membrane; Polysulfone; Polyvinylpyrrolidone; Ultrafiltration

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1. Introduction

In an organic composite membrane manufacture process via phase inversion, the characteristics of the prepared membranes depend on the used components [1,2]. These components are classified in three groups: polymer, additives and solvent.

The structure, morphology and characteristics of the membranes depend on the selection of polymer, solvents and non-solvents, additives, precipitation time, bath temperature and other parameters during immersion precipitation [3–6].

Apart from its chemical nature, the concentration of the casting polymer is very important in the process of membrane fabrication via immersion precipitation. Increasing polymer concentration in the casting

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solution produces membranes with low porosity and smaller pore size. In this case, the macrovoid formation is suppressed and the tendency to form sponge-like structures is enhanced. The UF membranes are obtained within a range of polymer concentration of 12–20 wt.% [7].

The selection of the solvent/non-solvent system also strongly affects the morphology and properties of casted membranes. A low miscibility of the polymer in the solvent leads to fabrication of a nonporous membrane, while more porous membranes are obtained when the miscibility is high. Usually, aprotic solvents—where there are no hydrogen atoms able to contribute to hydrogen bonding—are preferred for membrane casting. Aprotic polar solvents such as N-methyl-2-pyrrolidone (NMP), dimethyl formamide, dimethyl acetamide or dimethyl sulfoxide are preferable for rapid precipitation (instantaneous demixing) upon immersion in the non-solvent water and this produces anisotropic membranes with a high porosity [8].

To improve the membrane morphology and properties, the addition of different inorganic and high molecular weight organic additives to casting solution have been reported by different authors [9–12]. Many researchers have attempted to explain the membrane-forming mechanism based on the changes in kinetic and thermodynamic properties during the phase inversion process when a suitable additive is introduced into the casting solution [13–15]. Commonly used additives can be classified into the following categories [16]:

1. Polymer additives (PVP and PEG).
2. Low-molecular-weight chemicals including salts (LiCl), inorganic acids (acetic acid and phosphoric acid), organic acids (propionic acid).
3. Weak co-solvents (ethanol, propanol and acetone).
4. Weak non-solvents (glycerol and ethylene glycol).
5. Strong non-solvents such as water.

An additive can function as pore former, increasing solution viscosity or accelerating the phase inversion process. For example, the effect of LiCl addition in the membrane formation has been investigated in several studies [9,10,13–15,17–20]. Fontananova et al. [9] found that LiCl addition in the PVDF/ dimethylacetamide dope increases flux of the casted membranes at low LiCl concentration (2.5 wt.%) but suppresses macrovoid formation at a high concentration (7.5% LiCl) and results in a decrease of the membrane permeation flux. Similar results were obtained by Ahmed et al. [17] and Shi et al. [10], who showed that LiCl addition at a concentration lower than 4 wt.% improved both the flux and rejection rates. On the other hand, LiCl interacts strongly with the polymer and solvent, as demonstrated by the significant increase in viscosity of LiCl enhanced casting solutions [10,13,14].

Saljoughi et al. [21] reported that an increase of PVP concentration in the cast film from 0 to 1.5 wt.% resulted in the facilitation of macrovoid formation in the membrane sub-layer, which increased pure water flux. Wang et al. [22] showed that the PVP-added PES membrane had a higher water flux and lower water contact angle than the neat PES membrane. Ochoa et al. [23] proved that the addition of PVP to the casting solution increased the UF PES membrane permeability with no significant changes in selectivity.

Han and Nam [24] and other authors [10,25] recorded an increase of the casting solution viscosity with PVP addition. Matsuyama et al. [26] showed that PVP with higher molecular weight leads to formation of a sponge like structure.

Marchese et al. [27] reported that the reasons behind the increase in membrane permeability when PVP is added are an increase in the pore density, a decrease in the effective thickness of the dense layer due to macrovoids in the support layer and an increase in the hydrophilicity of the surfaces on the membrane eliminated surfaces and inside the pores. The phenomena of macrovoids formation, which are large elongated spaces below the upper surface of the membrane, have been widely discussed by different authors [3,28,29].

In this work, polysulfone was used as polymer (Fig. 1). This polymer is commonly used in membrane development due to its thermal and chemical stability and mechanical strength [30]. However, these membranes have the disadvantage of being hydrophobic in nature and it is proved that hydrophobic membranes are more prone to fouling than hydrophilic ones [31]. In fact, membrane fouling is the main problem during ultrafiltration processes since it causes flux reduction [32]. Aside from the membrane material, the fouling tendency is also influenced by membrane pore structure and surface roughness [33]. Nevertheless, these problems, as previously discussed, can be reduced by

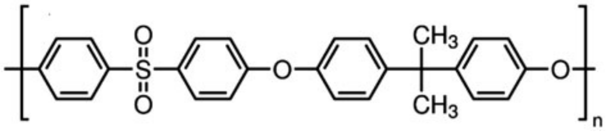


Fig. 1. Chemical structure of polysulfone.

adding some hydrophilic functional polymers, or other types of additives, in order to increase the hydrophilicity of this kind of membranes [34,35].

The novelty of this work is that two different additives, polyvinylpyrrolidone (PVP) (Fig. 2) [36–38] and lithium chloride [30,39,40], were used to respectively increase the permeability of the polysulfone membrane and maintain a narrow pore size range, these being the desired properties for a membrane to be used in water treatment. NMP was used as solvent for the development of all membranes due to its low toxicity [41] and aprotic polar character. Several experimental tests for membrane casting were established in order to evaluate the effect of the polymer concentration and additives addition on the characteristics of the prepared membranes.

2. Experimental

2.1. Materials

Polysulfone (Lasulf natural 0030) was supplied by Lati Ibérica S.L., PVP by Sigma and NMP by Riedel de Häen. Membrane support was a non-woven polyester film, with a 128 µm thickness, supplied by Ahlstrom MT. Moreover, 15–20 kDa (Fluka), 70 kDa (Fluka) and 148 kDa (Sigma) dextrans were used in the retention tests for membranes characterization.

2.2. Instruments

The casting solutions were perfectly mixed using an overhead shaker (Reax 20, Heidolph) and their viscosity was measured by a Brookfield viscometer (Model LVDVI). Fig. 3 shows the automatic film applicator coater (ZAA 2300, Zehntner) where membrane casting took place. Average membrane thickness was measured using a Mitutoyo 293–801 digital micrometer. Permeation tests—to calculate the permeability—and retention tests with dextrans—to determinate the molecular weight cut off (MWCO) of the membranes [42–44]—were carried out using a stirred batch cell (Amicon) and a stirred stainless steel ultrafiltration cell (Osmonics) respectively. The concentration of dextrans was determined by measuring the organic carbon concentration in the feed and the permeate stream, using a total organic carbon analyzer (VCSH model, Shimadzu). The surface morphology of the membranes was characterized by atomic force microscopy (AFM) (Nanotec) and Scanning Electron Microscopy (SEM) (EVO 50XVP, Zeiss). Membrane samples were coated with gold before SEM examination. The spectra of the different functional groups of the membranes were recorded by Attenuated Total Reflection - Infrared Spectroscopy (ATR-IR) in the range of wave numbers 4,000–600 cm^{-1} using a Shimadzu MIRacle 10 FT-IR spectrometer.

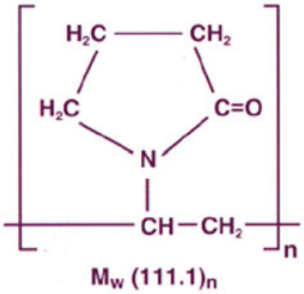


Fig. 2. Chemical structure of PVP.

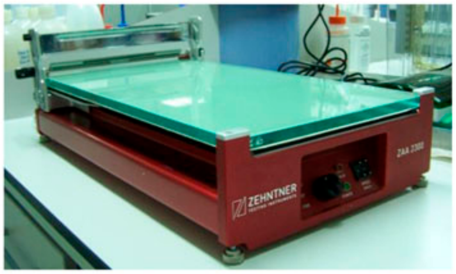


Fig. 3. Automatic film applicator coater.

2.3. Preparation of porous membranes

In order to assess the influence of the polymer and the different additives, on the prepared membrane characteristics, several sets of experiments were carried out, as shown in Table 1. The first set (M1 and M2.1, M2.2, M2.3 six experiments) was intended to test the effect of varying concentrations of polymer and additives. The second set (M2, five experiments) was aimed to test the effect of different additives at the same polymer concentration. With the third set

Table 1
Casting membrane composition

Membrane code	Membrane composition
M1.1	18% PS, 4% PVP, 0% LiCl, 78% NMP
M1.2	18% PS, 2% PVP, 2% LiCl, 78% NMP
M1.3	18% PS, 0% PVP, 4% LiCl, 78% NMP
M2.1	20% PS, 4% PVP, 0% LiCl, 76% NMP
M2.2	20% PS, 2% PVP, 2% LiCl, 76% NMP
M2.3	20% PS, 0% PVP, 4% LiCl, 76% NMP
M2.4	20% PS, 4% PVP, 2% LiCl, 74% NMP
M2.5	20% PS, 2% PVP, 4% LiCl, 74% NMP
M3.1	14% PS, 4% PVP, 4% LiCl, 78% NMP
M3.2	22% PS, 0% PVP, 0% LiCl, 78% NMP

(M1 and M3, five experiments) the aim was to compare membrane characteristics modifying polymer and additives doses but maintaining the same solvent concentration.

In all cases, the polymer dope solution was prepared by simultaneously dissolving the desired amount of polysulfone and additives. The reactants were mixed in the following order: solvent, additives and polymer. The mixture was carried out under controlled atmosphere conditions, in a glass bottle agitated until complete solution. The stirring time varied from a day to several weeks depending on the characteristics of the mixture for each membrane. Once the solutions were ready, the different membranes were prepared by a phase inversion process. Table 2 shows the viscosity of all casting solutions. A small amount of the casting solution was spread out onto the support (a polyester non-woven film) and an automatic film applicator coater with a casting knife of a 170 μm thickness was used. The casting speed (constant for all membranes) was set at 60 mm/s. After the casting, the membranes were immersed in the coagulation bath (deionized water) at 0–4˚C for 10 min. Finally, the membranes were immersed in a deionized water bath at room temperature for 48 h.

2.4. Membrane thickness

The thickness of the final dry membranes was measured, at five different points in each membrane sample, using a Mitutoyo 293–801 digital micrometer. The measuring range of the equipment was 0–25 mm with a resolution up to 0.001 mm.

2.5. Membrane permeability

The intrinsic permeability of each membrane (working area 44.17 cm^2) was determined in a stirred ultrafiltration cell (Amicon) by measuring the permeation flux at different pressures (from 0 to 2 bar) using deionized water as feed, at a constant temperature of 25˚C. Measures were made in triplicate. The cell was previously filled with distilled water at 0.5 bar to compact the membrane. Compaction was considered complete after three identical readings at 20 min intervals.

Table 2
Viscosity of the casting solutions

Membrane	Viscosity, Cps
M1.1	1,385
M1.2	2,410
M1.3	6,450
M2.1	2,320
M2.2	5,475
M2.3	11,770
M2.4	14,400
M2.5	54,167
M3.1	2,500
M3.2	2,261

2.6. Molecular weight cut-off

In order to determine the MWCO of the membranes, dextrans with an average molecular weight of 15–20, 70 and 148 kDa were used. Each dextran was dissolved in deionized water to obtain a final concentration of 200 mg/L. The solution was permeated through the Osmonics cell under 3 bar pressure (membrane working area 16.9 cm^2). Dextran concentration was determined by measuring the organic carbon concentration in the feed and permeate streams. The nominal MWCO is defined by the smallest molecular weight dextran for which 90% rejection occurred.

2.7. AFM and SEM

Membrane surface morphology was characterized using AFM (Nanotec). AFM was operated in force mode, with an approach/retractaction speed of 1 μm/s and 1 μm of piezo-movement. In this method, the probe tip scans across the sample surface being imaged and is in direct physical contact with the sample. The piezoelectric scanner maintains the tip at a constant force and the flexion is detected by the photodetector. Keeping the force constant, the tip follows the profile and records the surface topography. Equipment resolution is high, approximately 1 nm for the *XY* plane and about 0.1 nm for the *Z* plane.

The membrane area scanned was of 4 μm × 4 μm. The AFM probe was a SiO_2 contact AFM probe (Nanosensors) with a spring constant of 25 N/m and a thickness of 10 nm.

Membrane surface morphology (pore distribution and pore size) was analyzed with the scanning electron microscope Zeiss EVO 50XVP (Carl Zeiss: AG, Oberkochen, Germany). The samples were coated with a 5 nm gold-palladium (80:20) layer (EM SCD00 Sputter Coater, LEICA Microsystems).

2.8. Attenuated total reflection - infrared spectroscopy

The different functional groups of the membranes were recorded by ATR-IR technique in the range of 4,000–600 cm^{-1} wave numbers using a Shimadzu MIRacle 10 FT-IR spectrometer. A total of 20 scans

Table 3
Membrane actual thickness (Knife gap: 170 μm)

Membrane	Average thickness (with support), μm	Average thickness (without support)*, μm	*n***	Standard Deviation	Thickness reduction, %
M1.1	201	73	5	4	57.06
M1.2	183	55	5	3	67.65
M1.3	183	55	5	3	67.65
M2.1	183	55	5	3	67.65
M2.2	198	70	5	4	58.82
M2.3	185	57	5	3	66.47
M2.4	196	68	5	4	60.00
M2.5	238	110	5	7	35.29
M3.1	180	52	5	3	69.41
M3.2	165	37	5	2	78.24

*Support thickness: 128 μm.
**Number of analyzed samples.

Table 4
Calculated intrinsic permeability and MWCO of the membranes

Membrane	Permeability, L/hm^2 bar	MWCO, kDa
M1.1	1.976	MWCO > 148
M1.2	1.575	MWCO > 148
M1.3	0.319	MWCO > 148
M2.1	0.788	70 < MWCO < 148
M2.2	0.219	MWCO < 15–20
M2.3	–*	–
M2.4	0.772	MWCO > 148
M2.5	–*	70 < MWCO < 148
M3.1	1.705	MWCO > 148
M3.2	0.027	15–20 < MWCO < 70

*The permeate flux was negligible at a 2 bar pressure.

were performed at a resolution of $4\,cm^{-1}$ using a diamond crystal; the temperature was 21 + 1˚C. No pre-treatment of the sample was needed.

3. Results

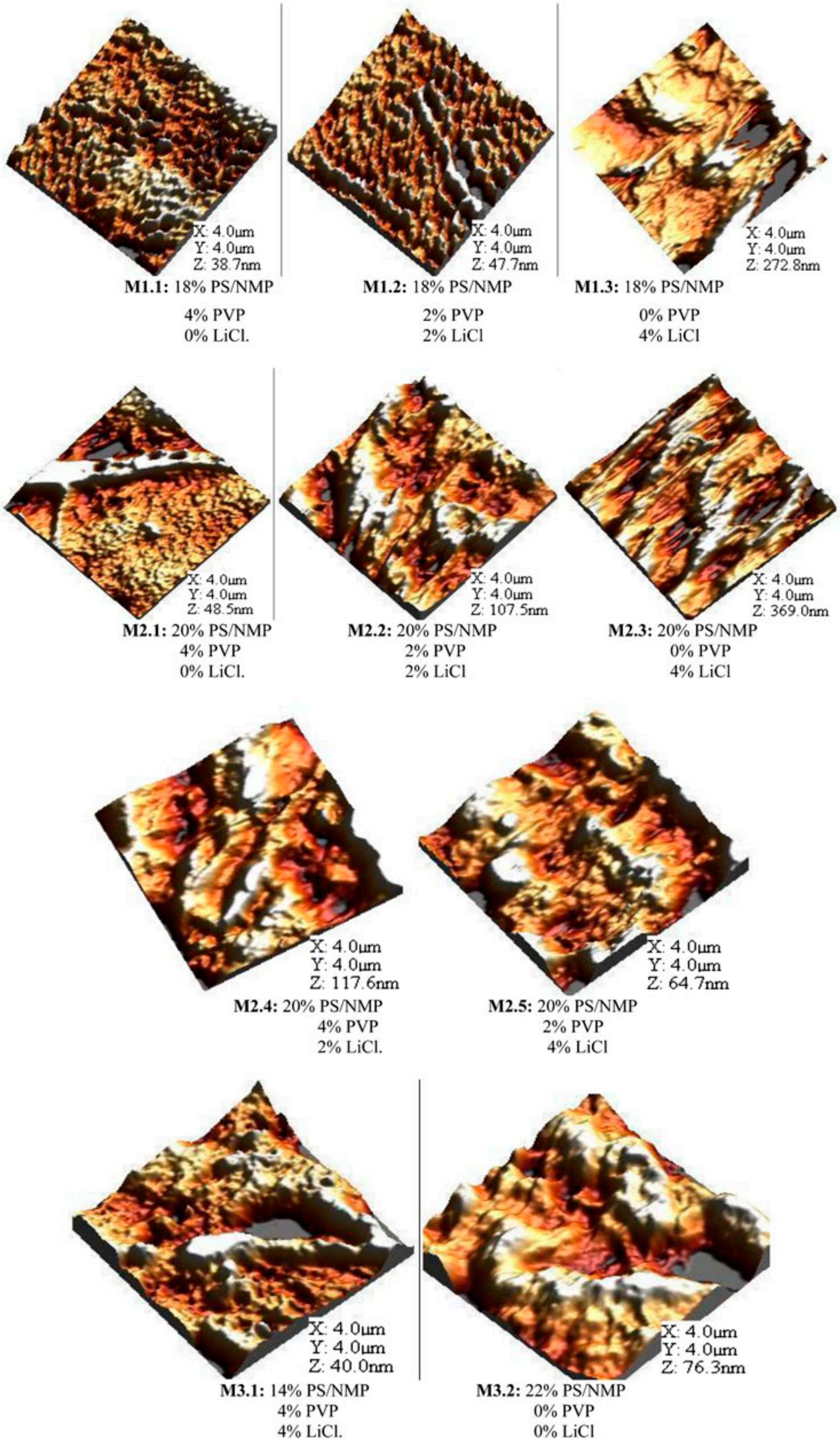
3.1. *Influence of additives in the casting-solutions*

The viscosity of the prepared solutions varied substantially with the amount of additives (lithium chloride and PVP) and polymer used. The smallest value was recorded for membrane M1.1 (1,385 Cps) and the largest for the M2.5 (54,167 Cps).

As shown in Table 2, differences in membrane composition between M2.1 and M2.4, as well as between M2.2 and M2.5, resided only in 2% of the LiCl amount added. In both cases, a very significant increase in viscosity for the membranes with a higher percentage of LiCl was confirmed. The significant enhancement of membrane viscosity caused by the addition of LiCl has been previously reported by several researchers [1,14,18]. This behavior can be attributed to the formation of acid–base complexes between LiCl and solvent, as well as to the interaction between Li^+ cation and electron donor in the polymer molecule.

Solution viscosity was also enhanced by PVP addition, as can be seen comparing results obtained between membranes M2.3 and M2.5, and between M2.2 and M2.4. This fact has been recorded by different authors [10,26] who have also observed a larger viscosity increase when using higher molecular weight PVP.

As was expected, higher solution viscosities were directly correlated with higher polymer concentrations, as shown by comparing results between



M1.1: 18% PS/NMP
4% PVP
0% LiCl.

M1.2: 18% PS/NMP
2% PVP
2% LiCl

M1.3: 18% PS/NMP
0% PVP
4% LiCl

M2.1: 20% PS/NMP
4% PVP
0% LiCl.

M2.2: 20% PS/NMP
2% PVP
2% LiCl

M2.3: 20% PS/NMP
0% PVP
4% LiCl

M2.4: 20% PS/NMP
4% PVP
2% LiCl.

M2.5: 20% PS/NMP
2% PVP
4% LiCl

M3.1: 14% PS/NMP
4% PVP
4% LiCl.

M3.2: 22% PS/NMP
0% PVP
0% LiCl

Fig. 4. AFM images of the obtained polymeric membranes.

Table 5
Membrane surface roughness

Membrane	Roughness (Z) (nm)
M1.1	38.7
M1.2	47.7
M1.3	272.8
M2.1	48.5
M2.2	107.5
M2.3	369.0
M2.4	117.6
M2.5	64.7
M3.1	40.0
M3.2	76.3

membranes M1.1 and M2.1, as well as between M1.2 and M2.2. In both cases, additives concentration had a larger effect on the viscosity than polymer concentration. In this sense, LiCl increased the viscosity of the casting-solution to a greater extent than PVP.

Rergarding the final thickness of the membranes, the smallest reduction was recorded for membrane M2.5, with the highest viscosity of the casting solution, whereas the highest reduction was recorded for membrane M3.2 which had the highest polysulfone concentration and no additives.

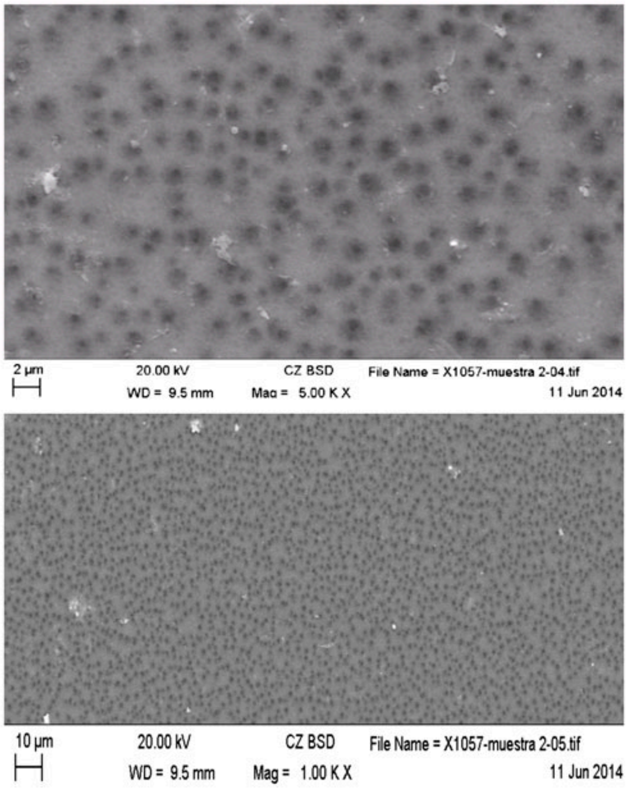


Fig. 5. SEM images of the M1.2 membrane at two different magnifications: (× 5,000) up and (× 1,000) down.

According to the results shown in Table 3, with a standard knife thickness of 170 μm, the range of the final thickness reduction—except for the membrane M2.5—was between 57.06 and 78.24%. A decrease in the effective thickness of the dense layer after adding PVP, due to the formation of macrovoids, has been previously reported by Marchese et al. [27].

3.2. *Influence of membrane composition on the intrinsic permeability*

Table 4 shows hydraulic permeability results recorded for the casted membranes. For membranes M2.3 and M2.5, permeability could not be measured as the flux was negligible at the highest used pressure of 2 bar. Highest permeability values were recorded for membranes with the highest molecular cut-off. Membrane M1.1 (18% PS, 4% PVP, 0% LiCl) achieved the highest permeability, followed by M3.1 (14% PS, 4% PVP, 4% LiCl) and M1.2 (18% PS, 2% PVP, 2% LiCl). All of these membranes had a cut-off higher than the largest used dextran (> 148 kDa).

Also according to Table 4, PVP effectively raised membrane permeability. Different authors have previously reported this behavior, reviewed by Lalia et al. [7]. Marchese et al. [27] showed that the reasons behind the increase in membrane permeability when PVP was added are an increase in pore density, a decrease in the effective thickness of the dense layer due to macrovoids in the support layer, and an increase in membrane surface and pore hydrophilicity. In order to verify the increase in hydrophilicity with PVP addition, contact angle measures would have to be performed.

Regarding the use of lithium chloride, results are in accordance with those reported by Fontanonova et al. [9]. The addition of LiCl at low concentrations increased flux of the casted membranes, whereas at high concentration, it suppressed macrovoid formation and resulted in a decrease of the membrane permeability.

Finally, from the comparison of the results obtained for M1.1 and M2.1 membranes, an apparent correlation can be established where membrane permeability decreases with polymer concentration. This would be explained by the fact that higher polymer concentrations cause an increase in the viscosity of the casting solution, and therefore the membrane presents a denser structure and smaller pore size, which reduces its hydraulic permeability [45–47].

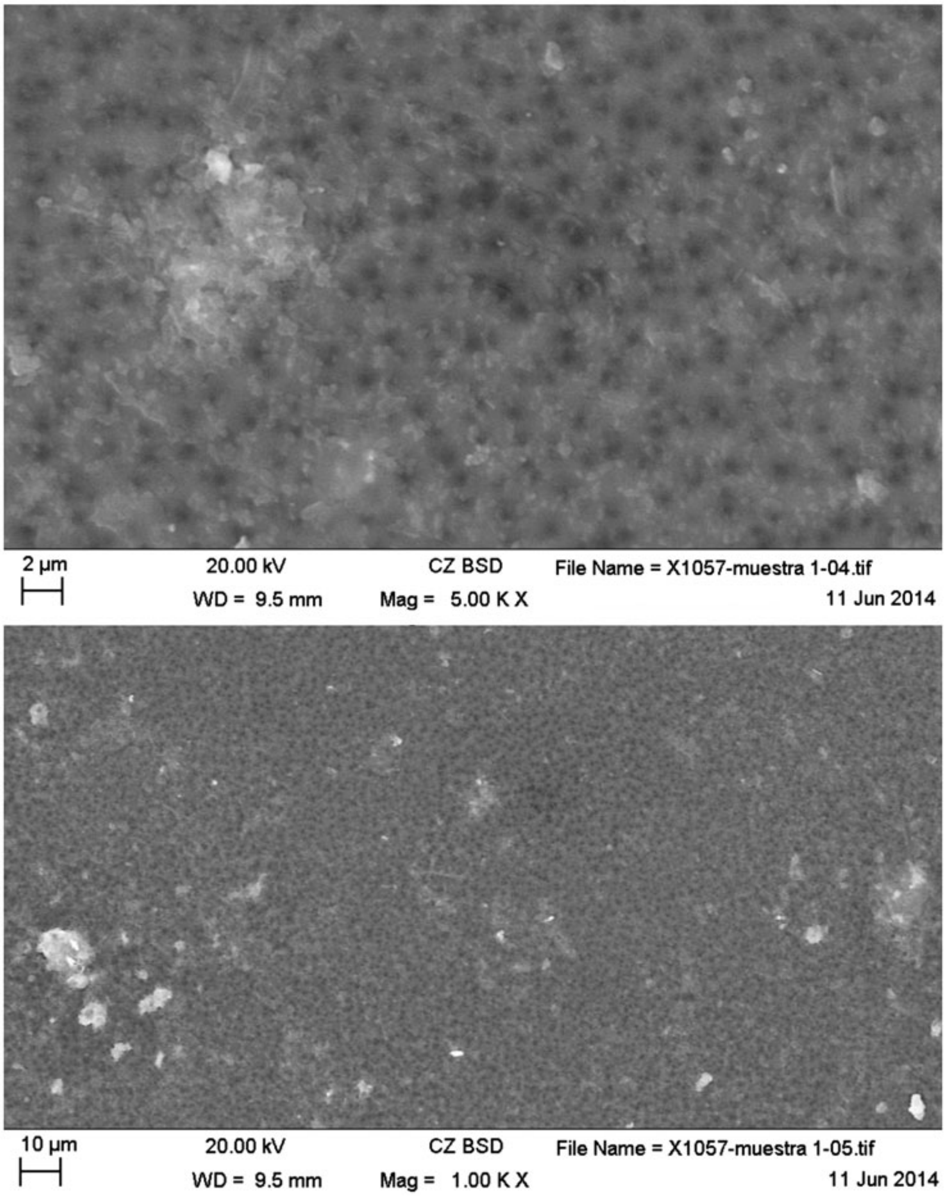


Fig. 6. SEM images of the M1.1 membrane at two different magnifications: (× 5,000) up and (× 1,000) down.

3.3. Influence of membrane composition on the MWCO

Results shown in Table 4 indicate that the higher the concentration of polysulfone, the smaller the range of the MWCO. The smallest cut-off was achieved for membrane M2.2. The value for M2.3 could not be measured as no flux was obtained at 3 bar pressure. Although polymer concentration had a greater influence than additive concentration, the amount of lithium chloride showed a significant influence on MWCO according to the results obtained for M2.1, M2.2 and M2.3 membranes. In this regard, the greater the concentration of lithium chloride, the smaller the range of the MWCO achieved. For the three M1 membranes, no conclusion could be achieved because the cut-off was in all cases higher than the largest dextran used.

3.4. Influence of membrane composition on the AFM images

Surface appearance and roughness for each membrane is shown in Fig. 4.

Table 5 shows membrane surface roughness information from the AFM analyses. As can be observed,

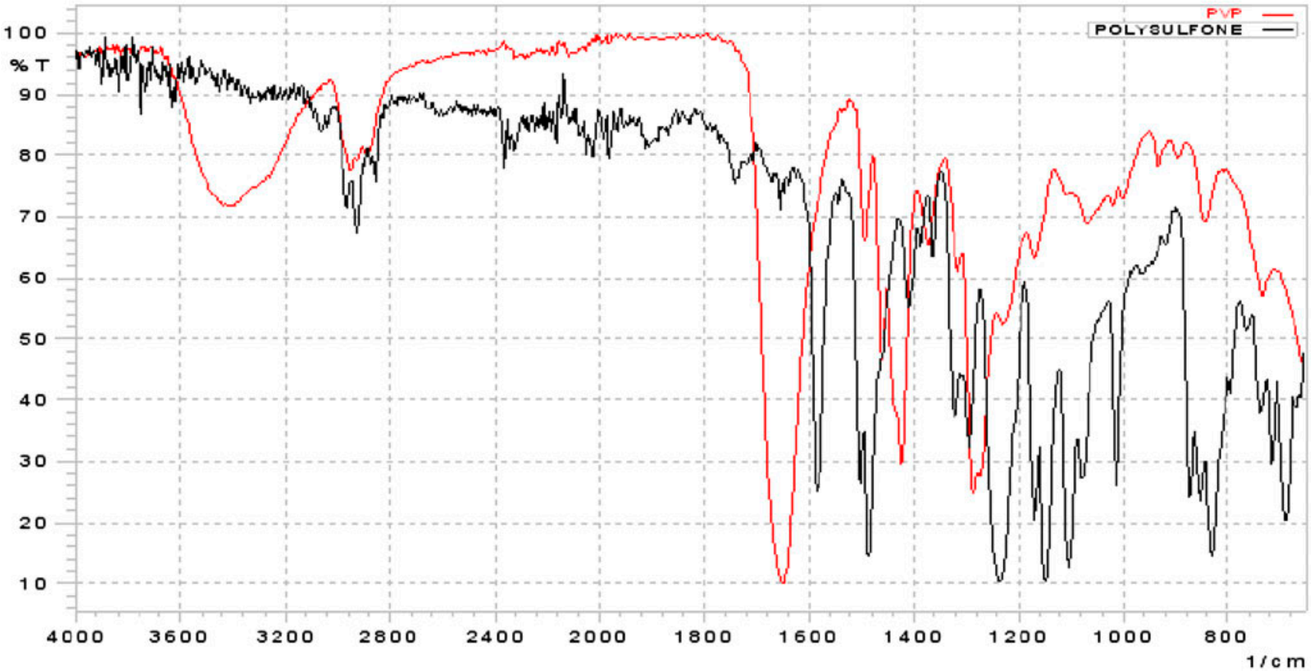


Fig. 7. FTIR analyses of the used compounds (PVP and polysulfone).

Table 6
Possible assignments of the IR spectra for the prepared membranes

Spectra assignments	Band frequency (cm^{-1})
O–H stretching	3,430
Aliphatic C–H stretching	2,870–2,950
Amide I, carboxilate, C=O stretching	1,600–1,660
C=C stretching in the aromatic rings	1,411–1,580
C–SO_2–C asymmetric stretching	1,323
S=O stretching	1,295
C–O–C symmetric stretching	1,240
C-SO_2-C symmetric stretching	1,157
Aliphatic C–C / aromatic C–H	1,080, 1,014
Bending, rocking	873
C–H rocking vibrations	635–855

the lowest value was recorded for M1.1 and the highest values for M2.3 followed by M1.3. Data varied substantially among membranes. Roughness increased with polysulfone concentration and appeared to increase with lithium chloride dose (according to results from M1.3, M2.3 and the comparison between M2.1 and M2.4), but decreased with PVP concentration (according to results from M1.1, M2.1 and the comparison between M2.3 and M2.5). However, these assumptions are not concluding since there are data in dissonance with them (results from M2.2 and M2.5 regarding the role of LiCl, and between M2.2 and M2.4 for PVP).

3.5. Influence of membrane composition on the SEM images

Figs. 5 and 6 show SEM images of two membranes surfaces. As can be observed, a high uniformity of pore distribution along the membrane surface was achieved. These images corroborate the results regarding MWCO and permeability. In this regard, M1.2 membrane showed the highest pore diameter, even higher than membrane M1.1. Moreoever, from the observation of the pictures it can be concluded that, rather than pores, they were pseudo-pores, since those values close to a 1 µm do not correspond to the permeability and molecular cut-off registered. They

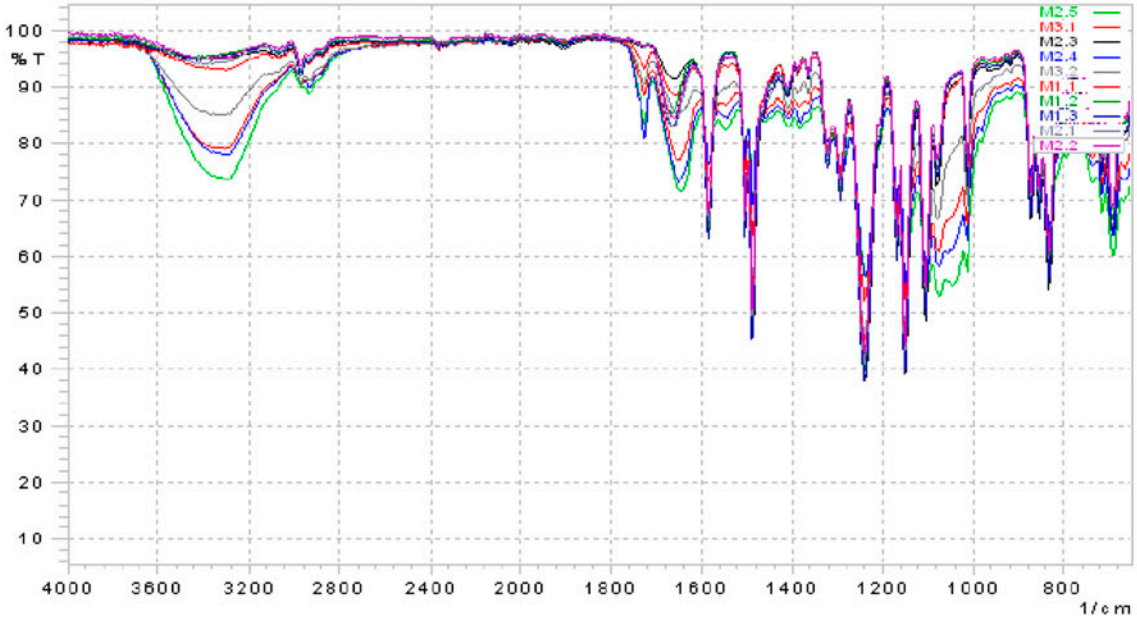


Fig. 8. FTIR analyses of the prepared polysulfone membranes.

would be essentially macrovoids underneath the thin surface [48].

3.6. Influence of membrane composition on the FTIR analysis

FTIR analyses were performed for all membranes, as well as for polysulfone and PVP (Fig. 7). Table 6 shows the main assignments of the IR spectra for the prepared membranes. As can be observed in this figure, two main differential peaks can be seen in the case of PVP at 3,300 and 1,650 cm^{-1} corresponding to hydroxyl group, and carbonyl, carboxyl, or amide I groups, respectively [22]. Significant differences are shown for the assayed membranes at 1,000–1,100, 1,660 and 3,300 cm^{-1} (Fig. 8). Membrane M2.5 (20% PS, 2% PVP and 4% LiCl) shows the highest peak at 3,300 cm^{-1}. However, due to the chemical composition of the solvent used NMP, and the reduced concentration of PVP in the final mixture, it is not possible to establish a correlation between these peak variations and the concentration and type of the additives used.

4. Conclusions

Results from this work corroborate that the use of additives like PVP and LiCl in polysulfone membranes can modify substantially the viscosity of the casting solution, the intrinsic permeability of the membrane, the range of the MWCO, and the roughness and thickness of the obtained membrane. Roughness of the prepared membranes increased with polysulfone concentration and appeared to increase with lithium chloride addition and decrease with PVP. A significant thickness reduction of the final prepared membranes was observed, which was lower for the membrane with the highest viscosity of the casting solution.

According to our results, to obtain a good ultrafiltration membrane for water treatment, it is necessary to add PVP at a low concentration (2–4%) to ensure a high pore density and consequently, a high permeability of the membranes with no significant changes in selectivity. On the other hand, LiCl at a low concentration (2–4%) increased the solution viscosity significantly and reduced macropore formation. This additive at low concentrations (≤ 4%) improved both the flux and rejection rate of the membrane. Neither the polymer nor LiCl concentrations should exceed 20 and 4%, respectively, since the resulting permeability would be too low for their application as ultrafiltration membranes in water treatment, even though a small pore size, would be preferable for a higher pollutant removal yield.

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