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Preparation and Flow Characterization of Polysulfone Membranes Modified with Nanoclay

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Abstract

Polymeric membranes have attracted interest in recent years for their unique properties in phase separation. Most polymers used in membrane synthesis are hydrophobic, which causes decrease in flux as well as membrane fouling, which therefore increases energy consumption and operational costs. Because the hydrophobic membrane surface absorbs nonpolar solutes and bio macromolecules that deposit in the membrane surface, filtration often leads to cake formation and membrane fouling. One alternative that has been studied in recent years to solve these problems involves membrane surface modification by coating, grafting or blending hydrophilic materials, thereby changing the surface properties and improving the membrane's performance. This work provides an approach to prepare polysulfone (PSf) ultrafiltration membranes by wet-phase inversion method using polysulfone solutions in N-methyl-2-pyrrolidone (NMP) containing different amounts of nanoclay as a surface modifier. The main objective was to study the effects of the nanoclay addition in contents of 1.0 to 5.0 mass% in the preparation of membranes, and to compare the resulting hydrophilic properties with non-modified PSf membranes.

One approach to reduce the occurrence of fouling is the surface modification method, which consists of the use of a hydrophilic component to increase the membrane surface's hydrophilicity. Among the methods of modification, the most common approach is the blending method because it can be done during membrane synthesis using different concentrations of the hydrophilic component.

Some researchers examined the use of clay minerals and clay-like materials such as montmorillonite as the inorganic component to modify the membrane surface. These clays are hydrophilic and present a high cationic exchange capacity and are easily expansible, allowing them to be intercalated with a wide range of organic species. Membranes prepared with the addition of clay in the casting solution showed improved hydrophilicity as well as thermal and mechanical resistance due to changes in the membrane structure formation.

Experimental

In this study, modified and unmodified PSf membranes were prepared via phase inversion method in order to evaluate their flux. Demineralised water was used as feed to carry out a filtration experiment, comparing the performance of the modified membrane to the pristine PSf membrane.

Six different 200 mL solutions were prepared at room temperature (25 ± 2°C) for membrane synthesis: one solution without clay as a modifier and the other five solutions with clay concentrations varying from 1.0 to 5.0% of polymer weight. These solutions were prepared by the dissolution of PSf (18 wt%) in 200 ml of NMP at room temperature in four steps. After adding the PSf, the solution was kept under stirring for 24 hours (180 rpm) and then kept in a vacuum before being cast onto a glass plate to release air bubbles. The solution was cast with a thickness of 130 μm in an automatic table using a cast knife on a glass substrate with casting speed of 1 cm/s. Thereafter, the glass substrate containing the film attached was quickly coagulated in a non-solvent (demineralized water) bath for membrane pore formation by phase inversion.

After being formed, the porous membranes were preserved in sodium disulfide solution before use.

The flux through the membrane was measured using a laboratory-scale dead-end ultrafiltration unit fed with deionized water, which flowed tangentially through the membrane surface under a pressure of 15 psi at room temperature. During one hour of experiment the volume of permeate was measured every five minutes and the flux, permeability, and hydraulic resistance were calculated. Four experiments were done with each membrane.

Results

The preliminary results (Table 1) show that the use of nanoclay improves membrane performance over that of pristine membranes. It was shown that the membranes composed of 4% clay demonstrated the highest flux and permeability, with moderate hydraulic resistance. It was observed that clay concentrations above 4% resulted in a lower flux and a higher hydraulic resistance, most likely due changes in internal membrane structure resulted from excessive clay addition. The validity of this hypothesis will be verified using Scanning Electron Microscopy technology, which will also help to understand the effect of nanoclay on membrane morphology.

Table 1.1 Results of the filtration experiment

	PS	PS 1%	PS 2%	PS3%	PS4%	PS5%
Flow (L/h)	0.504	0.332	0.426	0.743	0.808	0.315
Permeability (L/m² h kPa)	0.633	0.417	0.535	0.932	1.015	0.395
Hydraulic Resistance (kPa.s.m^{-1})	5.69×10^6	8.63×10^6	6.73×10^6	3.86×10^6	3.55×10^6	9.11×10^6

The next step in this study will be the comparison of these membranes in terms of hydrophilicity, rejection, microstructure, and physical properties contributing for a better understanding about modification process using clay as a modifying component.

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Figure
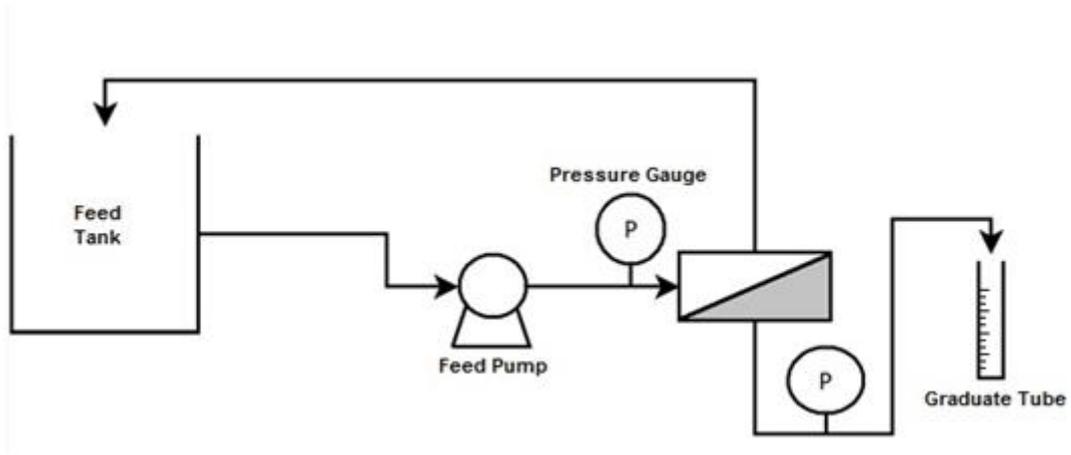
Fig 1. Cross-Flow ultrafiltration unit
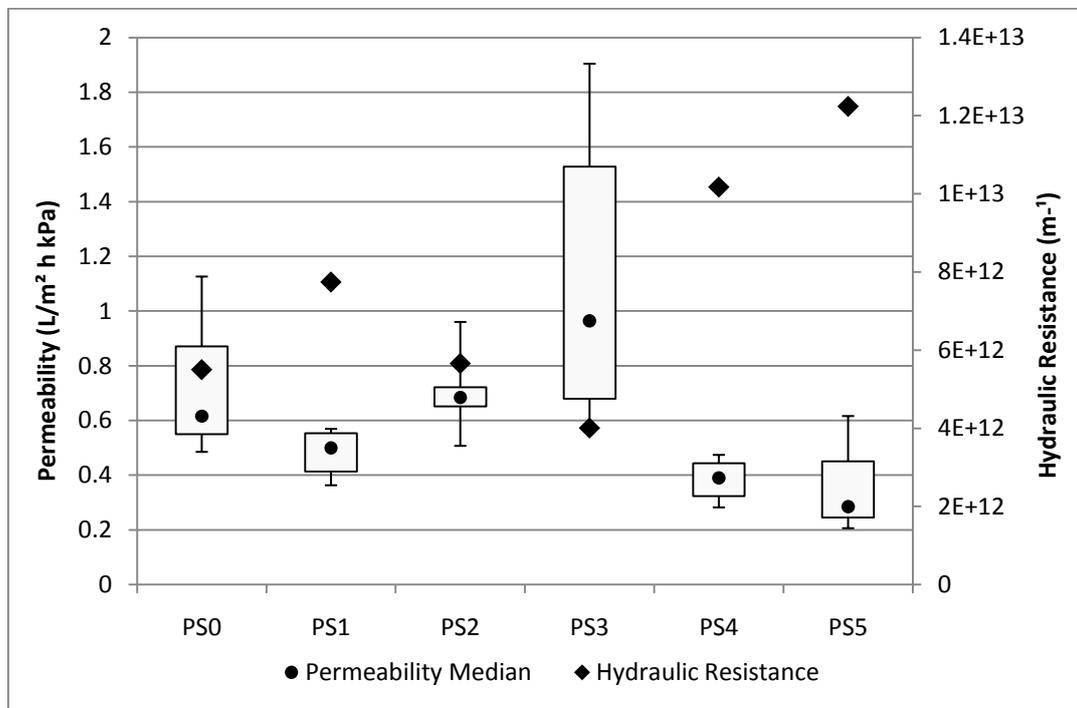
Fig 2. Cross-Flow ultrapure water permeability
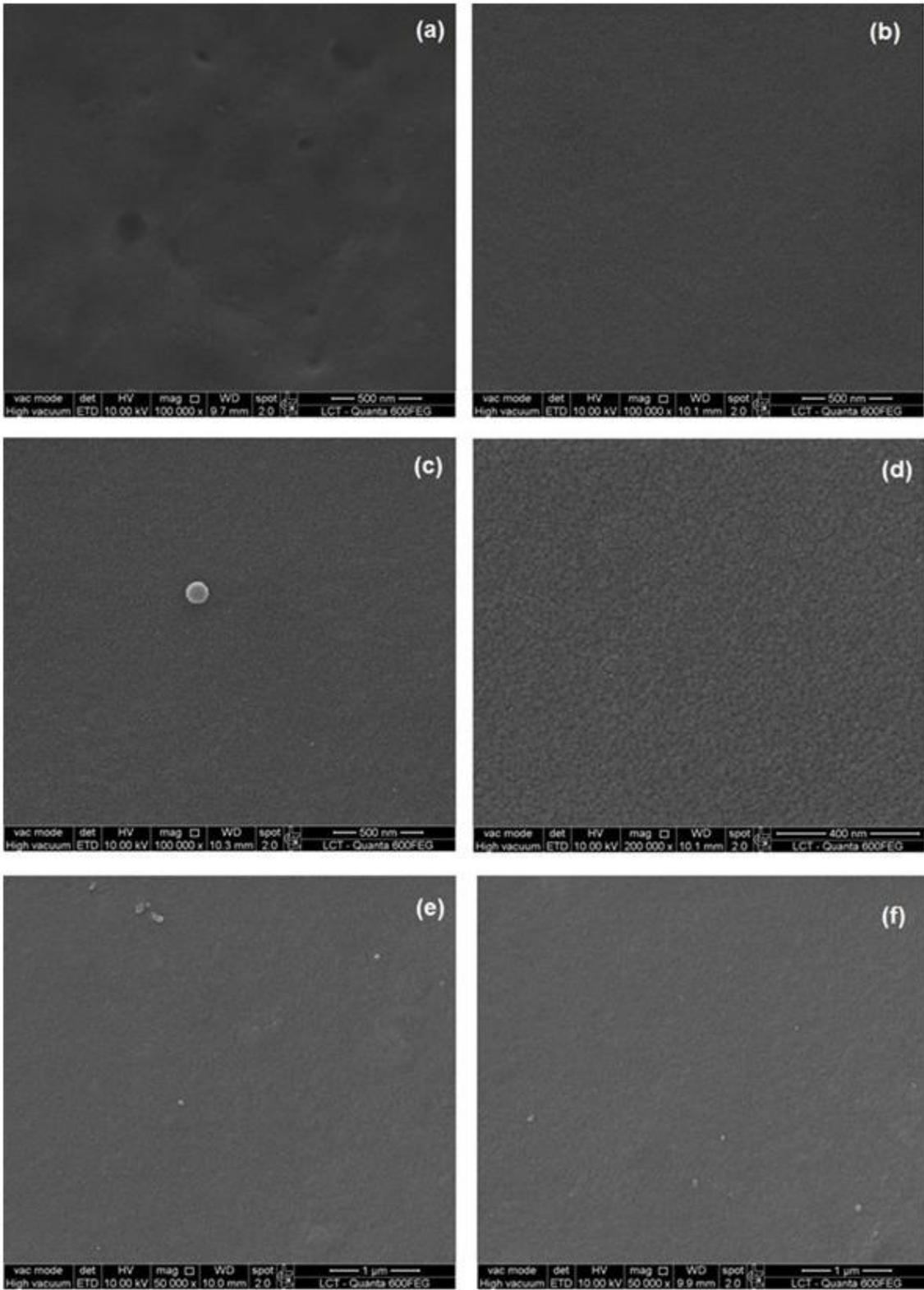
Fig 3. Contact Angle of PSf /clay membranes

Preparation and flow characterization of polysulfone membranes modified with nanoclay

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Abstract

Polymeric membranes have attracted interest in recent years because their peculiar properties in separation of solid-liquid, liquid-liquid and gas-liquid phases. Most polymers used in membrane synthesis are hydrophobic, which can result in reduced water flux due to membrane fouling, therefore increased energy consumption and operational costs. To overcome these problems, membrane surface modification by coating, or grafting or composite membrane preparation, for surface and internal structure properties modification, has extensively been used nowadays. Addition of inorganic nanoparticles in the polymeric dope solution is one of the most innovative approaches for obtaining high performance composite membranes. In order to understand the effect of inorganic nanoparticles additive on composite membranes performance, this work evaluated the use of clay nanoparticles as an additive for polysulfone (PSf) ultrafiltration membranes preparation. Dope solutions of 18% PSf/ N-methyl-2-pyrrolidone (NMP) containing different amounts (0 to 5 % PSf mass based) of clay nanoparticle (hydrophilic bentonite) were used for membrane cast using the phase inversion process. The results show that clay addiction on cast solution affected membrane morphology and performance. There was an improvement in membrane permeability to pure water when the clay concentration reached 3% compared to the neat membrane (1,104 x 0,742 $L.m^{-2}.h^{-1}kPa^{-1}$). Scanning Electronic Microscopy (SEM) images of membranes surfaces showed good clay nanoparticles dispersion in the range of 1 to 3%, but for higher concentrations clay nanoparticles started to aggregate, which was confirmed Energy Dispersive Spectroscopy (EDS) analysis. Preliminary results of using clay nanoparticles as an additive for composite membrane preparation are quite promising for obtaining membranes with improved performance.

Introduction

Membrane separation processes originated to meet different demands for colloidal/dissolved solids and liquid separation processes in different industrial sectors, such as chemical, petrochemical, metallurgical, food, pharmaceuticals, and electronics, which was subsequently expanded for water and wastewater treatment.

A membrane is considered effective if it successfully meets processes requirements cost-effectively. Usually the most common criteria to evaluate membrane performance are higher filtration flux with stable flux and lower filtration pressure, space saving, reliability in separation and high quality of produced water. Considering the large diversity of possible membrane materials, researchers are focusing on polymeric materials because of the better pore-forming control and lower cost compared to inorganic materials [1]. Among the materials used for membrane synthesis, polysulfone (PSf) is one of the most used polymeric materials. Some studies shows that

membranes made from PSf show notable oxidative, thermal and hydrolytic stability as well as mechanical resistance [2].

The main disadvantage of polymeric membrane for water and wastewater treatment is related to the hydrophobic properties of the polymers. Because polymeric membranes absorb nonpolar solutes and bio macromolecules, filtration often leads to membrane fouling. The fouling phenomena causes a decrease in rejection of target compounds associated with severe flux decline, which leads to an increase in energy consumption and therefore an increase in operational costs [3,4]. Considering these factors, membrane fouling is considered one of the main drawbacks for membrane application on a large scale. [4].

To reduce the occurrence of fouling, one of the current trends focus on membrane surface and morphology modification. Surface modification consists of using hydrophilic components to reduce membrane surface's hydrophobicity and thereby improve its performance. There are several methods to induce this hydrophilic surface modification such as coating, grafting and hydrophilic particles blending . The most common approach is the blending method. It is the most relevant from a practical standpoint, when compared to others available methods because it can be done during membrane synthesis using different concentrations of the hydrophilic components. [5]

Initially some studies for membrane modification tried to chemically modify the membrane surface by grafting hydrophilic monomers onto the membranes. Results showed that the effect was still too small to obtain the desired reduction of membrane fouling [6]. Other methods of modification include the usage of organic additives (polyvinylpyrrolidone or polyethylene glycol) [7-9] or the usage of inorganic dopant salts in dope solution to improve membrane's performance [9]

With the advance of nanotechnology research, these monomers were replaced by nanoparticles, which present unique chemical and physical properties compared to bulk particles. These nanoparticles can be incorporated within most polymeric materials by blending in the dope solution, producing membranes with enhanced flux and reduced fouling potential. The most common inorganic metallic nanoparticles used in membrane modification are colloidal-silver, iron, zirconium, silica, titanium and aluminum-based nanoparticles [1].

Other researchers examined the use of clay minerals and clay-like materials such as montmorillonite as the inorganic component to modify the membrane surface [10-15]. These clays are hydrophilic and present a high cationic exchange capacity and are easily expansible, allowing them to be intercalated with a wide range of organic species [13]. Results showed that membranes prepared with addition of clay in the dope solution improved the membrane hydrophilicity as well as thermal and mechanical resistance by affecting the membrane structure formation. [13-15]

In this work, nanoclay modified and unmodified PSf membranes were prepared via phase inversion method, which consists of casting a polymeric solution as a thin film and immersing it in a coagulation bath, facilitating the exchange of the solvent for the non-solvent and leading to asymmetric membrane structure formation. In order to evaluate flux and hydrophilicity of the modified membranes, contact angles were measured and pure water filtration experiments were carried out accordingly to compare the performance of the modified membrane to the pristine PSf membrane.

2. Experimental

2.1 Materials

Polysulfone UDEL® P-3500 LCD in pellets was provided by Solvay. Details of the polymers physical properties can be found in the manufacturer's website [16]. The

solvent N-methyl-2-pirrolidone (NMP) was bought from LabSynth and was used without further purification. Ultrapure water produced in a two-steps reverse osmosis system was used as non-solvent. The nanoclay (hydrophilic bentonite), with ≤ 25 micron average particle size and 180.1 gmol^{-1} molecular weight, was bought from by Sigma Aldrich [17]

2.2 Membrane Synthesis and modification

Six different 200g solutions were prepared at room temperature (25 ± 2°C) for membrane synthesis: one solution without clay as a modifier and the other five solutions with clay concentrations ranging from 1.0 to 5.0% of polymer weight, as shown in table 2.1. These solutions were prepared by the dissolution of PSf (18 wt%) in 200 ml of NMP at room temperature in four steps. After adding the PSf, the solution was kept under stirring in a mechanical stirring Fisatom 713D for 24 hours (180 rpm) and then kept in a vacuum for air bubbles releasing before being cast onto a glass plate.

Table 2.1 Membrane cast solution compositions

Membrane	Dope Solution (g)	NMP (g)	PSf (g)	Clay nanoparticles (g)
PS0	200	164	36	0
PS1	200	164	36	0,36
PS2	200	164	36	0,72
PS3	200	164	36	1,08
PS4	200	164	36	1,44
PS5	200	164	36	1,80

Membranes were cast using an adjustable casting knife Elcometer 3700 with 130 μm thickness in an automatic table Elcometer K4340M10 with casting speed of 1 cm/s. Thereafter, the glass substrate containing the film attached was quickly coagulated in a non-solvent (demineralized water) bath for membrane pore formation by phase inversion. After being formed, the porous membranes were kept in water bath for 24 hours to remove any residual solvent. After this, the membranes were preserved in sodium disulphide solution before use.

The membranes that weren't tested just after being produced were kept in isopropyl alcohol for 24 hours and then kept in controlled environment for drying naturally and prevent pore collapsing [9].

2.3 Membrane Characterization

The flux through the membrane was measured by using a laboratory-scale cross-flow ultrafiltration unit fed with distilled water, which flowed tangentially through the membrane surface under a pressure of 15 psi at room temperature as showed in Fig 1. The system had two pressure gauges in order to measure transmembrane pressure and permeate flow was measured using a graduate cylinder and a stopwatch.
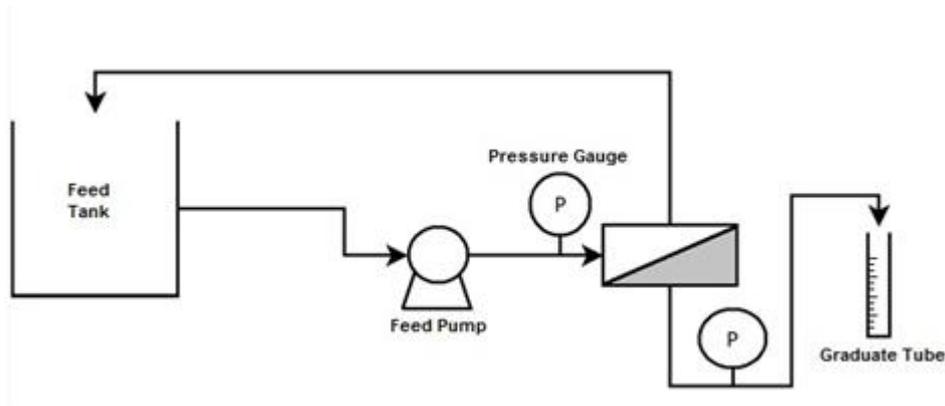
Fig 1. Cross-Flow ultrafiltration unit

During one hour of experiment the volume of permeate was measured every five minutes and the membrane permeability was calculated by Eq.(1)

$$P = \frac{J}{\Delta P} \qquad (1)$$

where J is the flux though membrane [L/h.m²], and ΔP the transmembrane pressure [kPa].

Considering the permeability, and the viscosity of ultrapure water used as feed the membrane hydraulic resistance was calculated as shown in Eq. (2)

$$P = \frac{1}{\mu_w . R_M} \qquad (2)$$

where μ_w is the viscosity of ultrapure water [Pa.s], P is the membrane permeability [m³/m².s.Pa] and RM is the membrane hydraulic resistance [m^{-1}]

The membrane hydrophilicity was determinated by measuring the contact angle using a goniometer (Krüss). Droplets of 2 μL of distilled water were dropped in completely dry membranes and the contact angle was measured after one minute at room temperature, according to the ISO 15989 [18]. At least 10 measurements were taken and the average was reported in order to get a more reliable value.

The membranes were analysed using SEM images in the efforts to correlate the results of permeability and hydrophilicity with surface modifications. The SEM operated with secondary electrons detection mode with 10 kV of accelerating voltage. The samples were coated with platinum in order to increase conductivity.

3. Results and Discussion

3.1 Membrane Permeability and Hydraulic Resistance

The results of the samples' permeability are showed by category in Fig 2. Membranes with 1% of clay presented lower permeability comparing to the non-modified ones. The increase of the clay content improved the flow rate and permeability for 2 and 3% membranes, but for concentrations higher than this the observed effect was the opposite: 4 and 5% clay membranes presented lower permeability and therefore higher hydraulic resistance (twice as much for 5% clay content compared to the neat membrane).

One possible explanation for the observed effect of higher clay concentration is that the additive could have caused a rapid demixing during coagulation due to high rates of water influx, resulting in membranes with sponge-like structure and lower

permeability. Another hypothesis is that the higher concentrations of clay make its dispersion more difficult, resulting in aggregates that can cause lower pore plugging and lower water permeability.
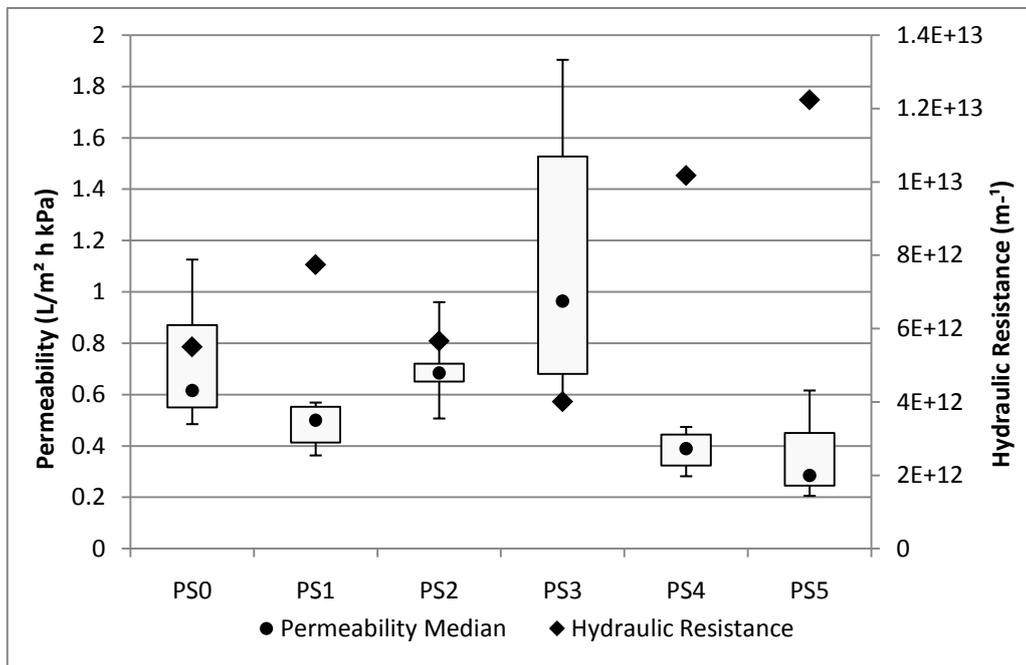
Fig 2. Cross-Flow ultrapure water permeability

3.2 Membrane Hydrophilicity

Membrane hydrophilicity, measured by contact angle, is an important parameter which can indirectly be related to membrane/contaminant interaction potential. In most cases higher membrane hydrophilicitycorrelates to a lower contact angle [12,15]. Contact angle is one of the tests commonly used for membrane characterization, but its results alone cannot be used to predict membrane performance. Results of contact angle tests are useful as complementary information to analyze data related to permeability and membrane superficial and internal microstructure [9]

Results of contact angle measurements of PSf/clay membranes with different clay contents are shown in Fig 3. It can be seen from Fig 3 that the contact angle changed slightly between the different membrane categories. Membranes with 2% clay content presented lower contact angles, but their permeability was similar to that of membranes without clay. This can be explained by the surface porosity and the presence of pores that are not connected to the other side of the membrane. This hypothesis, however, must be confirmed by cross-section SEM images.

Comparing the membranes without clay and the ones from 1 to 3% of clay content, they had similar contact angle measurements. The modified membranes, however, had lower values. The membranes with 4 and 5 % clay had higher values of contact angle, which correlates to a greater hydrophobicity. These results are compatible with the pure water flux in permeability test. Table 3.2.1 presents the average results for permeability, hydraulic resistance and contact angle for all membrane categories.

Table 3.2.1 Results of average membrane's permeability, hydraulic resistance and contact angle

Membrane	Permeability (L.m^{-2}.h^{-1}kPa^{-1})	Hydraulic Resistance (10^{+12} m^{-1})	Contact Angle (°)
PS0	0,742	5,50	82,8
PS1	0,483	7,75	82,1
PS2	0,704	5,66	81,9
PS3	1,104	4,01	82,0
PS4	0,384	10,2	86,1
PS5	0,369	12,2	87,4

Fig 3. Contact Angle of PSf /clay membranes

3.2 Superficial SEM images

The membrane surfaces were examined in detail by SEM with EDS detector. Figure 3 compares the images obtained with magnifications from 50k to 200k times. 50k magnification was used in membranes PS4 and PS5 to show clay aggregates in the surface. 100k magnification was used in other membrane's surfaces and 200k was used in PS3, which presented the best results in terms of permeability. Higher magnifications caused damages to membrane's surface, resulting in blurry images.

As can be seen in Fig 3, the PS0, PS1 and PS3 membranes displayed a good dispersion of polysulphone and clay (when applicable). It was noticed in some sections of the sample of PS2 some areas with aggregates like the one showed in Fig 3-c. The EDS detector was used to obtain aggregate's compositions. The main components were sulphur, carbon and oxygen, which is more likely to be polysulphone than clay, because silica and other mineral components were not detected.

The images for PS4 and PS5 presented more aggregates spread throughout the polymeric matrix. These aggregates were smaller and had irregular surfaces (differing from the polymeric aggregates found in PS2 sample). The EDS spectrum confirmed the presence of silica and aluminum (as well as carbon, sulphur and oxygen) showing that those aggregates were likely to be clay aggregates in a polymeric matrix.

PS3's micrograph, with 200k magnification, starts to show the membrane porosity that couldn't be seen in 100k magnification. Despite this, the porosity still couldn't be determined using image refinement software and further increases would damage the membrane's surface.
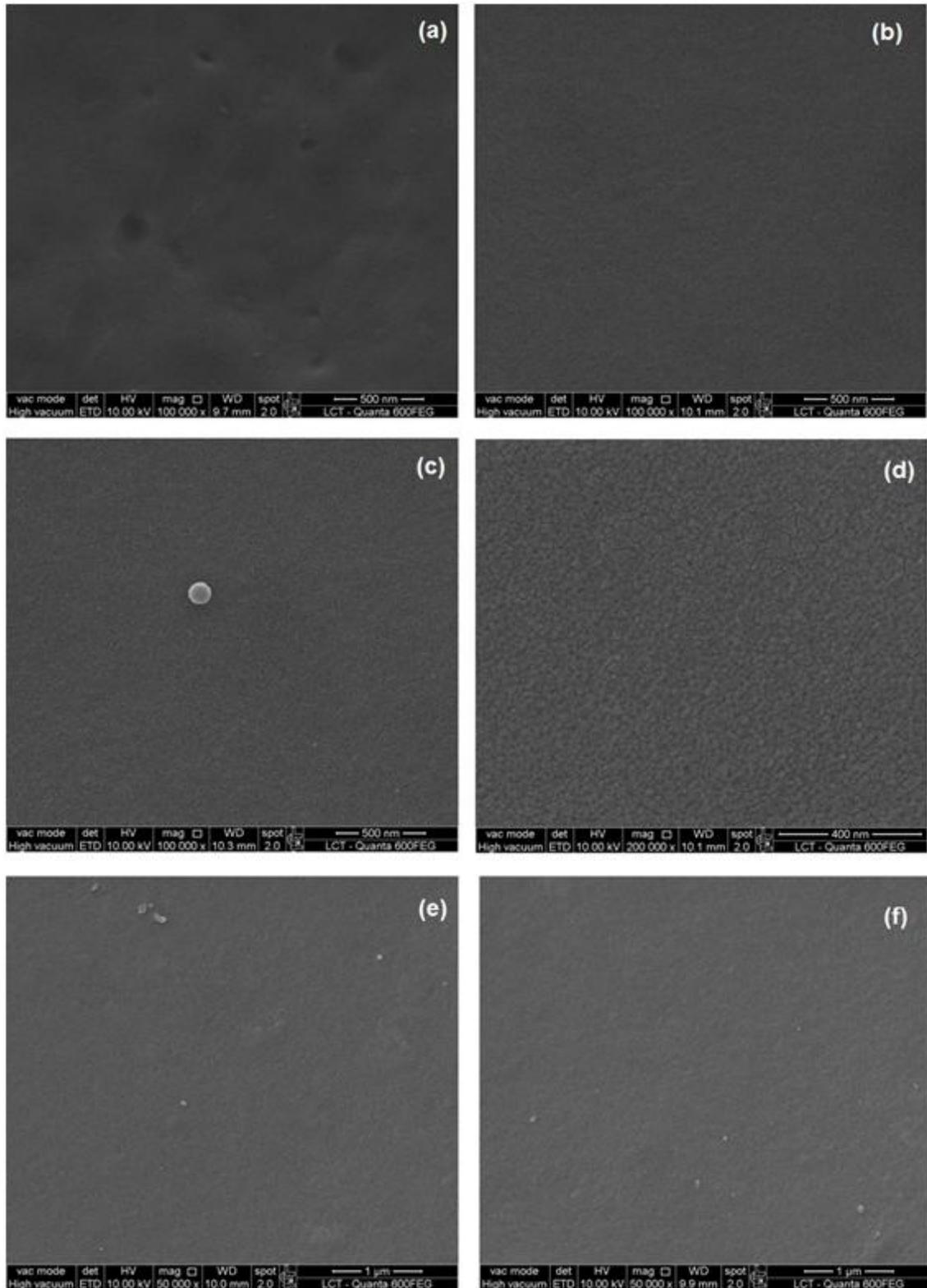
Fig 3. Micrographs of membranes' surfaces (a) PS0 and (b) PS1; (c) PS2, showing not dispersed polysulphone; (d) PS3; (e) PS4 and (f) PS5, showing clay aggregates.

4. Conclusions

The performance in terms of flux and the hydrophilicity of PSf membranes modified with blended clay nanoparticles were compared with that of a pure PSf solution. The same preparation conditions were used in the formation of all membranes in order to compare the effects of variation of clay concentrations in the dope solution.

The results showed that adding clay in the cast solution results in more hydrophilic membranes with higher pure water flux and permeability. For concentrations of 1 and 2% (in terms of polymer mass) the performance was very similar to the pure membrane. The contact angle of solutions containing from 0 to 3% were very similar. Although 1% clay membranes had lower average contact angles, their permeability was slightly lower compared to that of the neat membrane. Membranes with 3% clay content presented a notable increase in permeability, but their contact angles were similar to those of the categories below 3%. For concentrations above 3% the permeability decreased significantly and the contact angles were higher, indicating that those membranes became more hydrophobic.

The next step in this research will focus on a more detailed membrane performance evaluation in terms of rejection, cross-sectional microstructure, and physical properties. Analyzing the cross-section of the membranes can strengthen the hypothesis related to permeability behavior of high concentration clay membranes and help to comprehend the internal structure formation mechanisms. After those tests, the membranes will be tested to evaluate fouling conditions and the viability of using those clay modified membranes in water treatment systems.

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