CLAY NANOPARTICLES EFFECTS ON PERFORMANCE AND MORPHOLOGY OF POLY(VINYLIDENE FLUORIDE) MEMBRANES

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Abstract - In this study, a comparison between neat poly(vinylidene fluoride) (PVDF) membrane and composite (PVDF-Nanoclay and PVDF-PVP-Nanoclay) membranes is presented. All membranes were synthesized by the phase inversion process, using 18% PVDF, n-methylpyrrolidone as solvent and water as the non-solvent. Demineralized water cross-flow permeation tests were conducted to evaluate the membranes performance. Scanning electron microscopy (SEM) images of the membranes surface and cross-section and water contact angle measurements were used to estimate additives effects on membranes morphology. The results indicate that dopant addition affected membrane permeate flux and morphology. The 4% nanoclay composite membrane resulted in the highest ultrapure water permeability (0.9130 $m^3.m^{-2}.h^{-1}.MPa^{-1}$), lower hydraulic resistance ($3.27\times10^{+12}.m^{-1}$), lower contact angle ($87.1º$) and highest surface porosity (0.95%). Furthermore, it was verified that the membrane surface porosity increased with increasing clay nanoparticles concentrations. It was observed that the morphology of the membranes with clay nanoparticle addition is characterized by a thin surface layer, with macro-pores, a thin bottom layer, which has a sponge-like structure with micro-pores and a thick intermediate layer, with finger-like pores and macro-pores. It was also verified that the introduction of PVP promotes a denser morphology compared with membranes without it. Based on the SEM surface and cross-sectional images and permeability tests, it became evident that the internal pore morphology plays an important role in membrane performance, because the higher the frequency and extent of the finger-like pores in the intermediate layer the higher is the membrane permeability. These preliminary results indicated that the use of nanoclay as an additive for membrane casting is a promising procedure for improving membrane performance for water and wastewater treatment.
Keywords: Ultrafiltration; Clay Nanoparticles; Poly(vinylidene fluoride); Water Treatment; Performance; Morphology.

INTRODUCTION

Poly(vinylidene fluorine) (PVDF) is a semi-crystalline polymer. The main macromolecular straight chain of PVDF is surrounded by fluorine and hydrogen atoms ($-CH_2-CF_2-$). Its crystalline structure and spatial arrangement of CH_2 and CF_2 groups along the polymer chain result in excellent mechanical stability (Lui *et al*., 2011b). The high electronegativity of fluorine atoms and the high dissociation energy of the C–F bond provide a better thermal stability compared with hydrocarbon polymers (Lovinger and Reed, 1980). Furthermore, PVDF is chemically stable to a wide range of chemical products such as halogens,

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oxidants, inorganic acids and aromatic, aliphatic and chlorinated solvents (Hashim *et al*., 2011). These PVDF properties associated with its low price, radiation resistance, low surface energy and dielectric constant have made it one of the most popular and usual polymers for microfiltration (MF) and ultrafiltration (UF) membranes (Lui *et al*., 2007; Zhao *et al*., 2008).

However, despite the previously presented advantages, PVDF has an intrinsic hydrophobicity. Thus, PVDF membranes have limitations for water, sewage and aqueous mixtures treatment (Lui *et al*., 2007; Zhao *et al*., 2008), which restricts the use of this kind of polymer.

The PVDF membrane hydrophobicity results in low membrane wettability and higher resistance for water flow, because there are no hydrogen bonding interactions in the boundary layer between the membrane interface and water. Moreover, hydrophobic membranes are more susceptible to fouling during treatment of aqueous solutions containing natural organic matter (NOM) (Lui *et al*., 2011b). As water molecules repulsion by hydrophobic surfaces is a spontaneous process with an increase in entropy, NOM molecules have a tendency to adsorb onto the membrane surface (Brant and Childress, 2004; Du *et al*., 2009).

In order to incorporate hydrophilic proprieties into conventional hydrophobic PVDF membranes for better performance, several membrane modification methods have been explored (Zhao *et al*., 2008). The blending modification method is ordinarily used to obtain the desired functional properties during membrane synthesis. In this way, the synthesis and modification processes can be performed in only one step (Zhao *et al*., 2008). Until now, three main types of additives have been used for PVDF membrane modification: hydrophilic polymers or pore-forming (polyvinyl-pyrrolidone - PVP and poly(methyl methacrylate) - PMMA), amphiphilic copolymers (P(MMA-r-POEM) or P(MMA-r-PEGMA); PVDF-g-POEM; PVDF-g-PMAA; PVDF-g-PEGMA; PVDF-g-PAAc; PVDF-g-PAAc-b-PNIPAAM; PVDF-g-PTMASPMA and HPE-g-MPEG) and inorganic particles (TiO$_2$; SiO$_2$; Al$_2$O$_3$ and ZrO$_2$) (Liu *et al*., 2011b).

According to the results summarized in Liu *et al.* (2011b), the introduction of additives improved the pure water flux, increased the water flux recovery and decreased the contact angle. In most cases, exception made for P(MMA-r-POEM), HPE-g-MPEG and TiO$_2$, an improvement in the rejection rate was also observed when using additives.

In the past years, the addition of inorganic nanoparticles to polymer solutions has become an attrac-

tive method for polymeric membrane synthesis and has been extensively studied because of its simplicity (Yan *et al*., 2006). Research has focused on the preparation of composite or organic-inorganic hybrid membranes by the incorporation of inorganic nanoparticles. As explained previously, this blending modification is intended to improve porous membrane performance, reducing the hydrophobicity and increasing fouling resistance and permeability, which result from a better control of membrane surface properties and pore morphology (Yan *et al*., 2006; Lui *et al*., 2011b). This is possible because nanoparticles have unique properties (electronic, magnetic, optical, thermal and mechanical stability) and also due to their small size, high activity and high surface area (Yan *et al*., 2006).

Bottino *et al*. (2001, 2002) and Lin *et al*. (2003) have shown that PVDF- SiO$_2$ membrane morphology and elasticity are influenced by the mass of inorganic material. According to Cao *et al*. (2006), PVDF-TiO$_2$ membrane permeability and hydrophilicity show better results than simple PVDF membranes and also decreased median pore size and surface roughness. Cao *et al*. (2006) also conclude that TiO$_2$ nanoparticles had a strong effect on the PVDF molecule's crystallization.

Yan *et al.* (2006) have shown that the addition of Al$_2$O$_3$ nanoparticles did not affect pore size and numbers or the formation of crystals. The surface morphology was modified by increasing the surface roughness, but this did not affect the performance. According to the author, the contact angle decreased, as well as tensile strength, while rupture elongation improved.

According to Ma *et al*. (2012) and Monticelli *et al*. (2007), the addition of nanoclay to a polysulfone (PSf) membrane can increase water permeate flux. Monticelli *et al*. (2007) demonstrated that modified membranes had a higher contaminant rejection rate when compared to pure polysulfone membranes. Also according to the cited authors, the modified (PSf)-clay showed a lower contact angle; the clay increased membrane wettability at the same time that the mechanical properties were improved. On the other hand, Ma *et al*. (2012) showed that the nanoclay had little effect on the hydrophilicity of membranes and that it deteriorates to some extent the membrane mechanical properties. Ma *et al*. (2012) demonstrated that the addition of nanoclay to polysulfone membranes can increase the ratio of large pores in the skin layer and also the pure water flow. This may be due to a difference in the membrane composition. The aforementioned studies utilized different solvents, polymers and nanoclay concentra-

tions. Furthermore, MA *et al.* (2012) also used a pore forming additive PEG 400.

Anadão *et al.* (2010) also studied the incorporation of nanoclay in PSf membranes. Although water permeation tests were not performed, their results showed that hydrophilicity, thermal stability and mechanical resistance of the composite membranes were improved.

Mierzwa *et al.* (2013) and Ghaemi *et al.* (2001) argued that clay nanoparticles increased polyethersulfone membrane permeability and induced changes in the membrane surface and morphology. Ghaemi *et al.* (2001) indicated that, at all nanoclay concentrations added, higher membrane hydrophilicity, porosity and a thinner skin layer were obtained. According to Mierzwa *et al.* (2013), nanoclay addition increased the contact angle, reduced the negative surface charge density and had no effect on membrane porosity and thickness. However, there was an optimum clay nanoparticle concentration above which membrane performance was significantly reduced.

Considering the promising results obtained in the cited studies, the main objective of this work is to evaluate the effect of inorganic clay nanoparticles (hydrophilic montmorillonite) on the morphology and performance of poly(vinylidene fluoride) (PVDF) ultrafiltration membranes synthesized by the phase inversion process, compared to the neat PVDF membrane.

MATERIALS AND METHODS

Materials

Studies were conducted with commercial poly (vinylidene fluoride) (PVDF) Kynar Flex® 2821 (copolymer of poly(vinylidene fluorine) and hexafluoropropylene) kindly donated by *Arkema Química Ltda*.

N-methyl-2-pyrrolidone (NMP) with molecular weight of 99.1 g mol^{-1} was acquired from *Labsynth produtos para laboratórios Ltda* and was used as solvent.

The poly(vinylpyrrolidone) (PVP) with an average molecular weight of 10,000 g mol^{-1}, from Sigma Aldrich, was used as pore former.

The clay nanoparticles (Montmorillinite - Nanomer® PGV), pellets approximately 1 nm thick and with an aspect ratio (length/width) ranging from 200-400 and molecular weight of 180.1 g mol^{-1}, also from Sigma Aldrich, were used as additive.

All this chemicals were used as received. Demineralized water was prepared in the laboratory by double step reverse osmosis and used for membrane casting and membrane performance evaluation.

Solution Preparation and Membrane Casting Procedure

The reference solution was prepared with (PVDF) polymer at a fixed concentration (18% by weight) dissolved in N-methyl-2-pyrrolidone (NMP) solvent, at 50 ºC and stirred for 24 hours or until a homogenous polymeric solution was obtained using a mechanical stirrers (Fisaton 713D model).

For solutions with PVP, the final solution was obtained by the addition of 1% PVP (based on PVDF mass) together with PVDF. The PVP pore former addition was used to evaluate its combined effect on modified nanoclay membrane performance. For solutions containing clay nanoparticles (2% and 4% based on PVDF mass) specific amounts of clay were added and dispersed in the previously prepared solutions. The range of clay nanoparticle concentration chosen was based on previous results obtained by Mierzwa *et al.* (2013) and Ghaemi *et al.* (2011). This solution was stirred for 24 hours at 50 ºC for complete clay nanoparticle dispersion. Table 1 shows the composition of each solution prepared.

Table 1: Different composite PVDF membranes.

Membrane	PVDF (wt%)	NMP (wt%)	PVP (wt%)[1]	Clay nanoparticles (wt%)[1]
Control	18	82	0	0
0% PVP + 2% clay	18	82	0	2
0% PVP + 4% clay	18	82	0	4
1% PVP + 0% clay	18	82	1	0
1% PVP + 2% clay	18	82	1	2
1% PVP + 4% clay	18	82	1	4

[1] wt% is based on PVDF mass

Membranes were synthesized by the phase inversion process. Each final solution was spread onto a glass plate to produce a flat sheet membrane. The spreading itself was done using an automatic film applicator (ELCOMETER K4340 M10 model Automatic Film Applicator) coupled with bar coaters (ELCOMETER model 3700).

The polymeric film thickness adopted was 100 μm with a casting velocity of 4 cm/s. The polymeric film was immediately immersed into the coagulation bath (demineralized water) at 25 ºC, for 2 minutes or until the membrane was considered to be set. From the coagulation bath the cast membranes were transferred to another water bath (demineralized water at ambient temperature) for at least 24 hours to remove

any residual solvent. Table 2 shows the casting process parameters.

Table 2: Casting parameters for flat sheet membranes.

Casting Temperature	ambient
Casting knife	100 μm
Casting Speed	0.04 m/s
Coagulation Bath	demineralized water
Coagulation Bath Temperature	25 ºC
Coagulation Bath Time	2 minutes

Membrane Performance Evaluation

For performance evaluation, demineralized water flow tests were conducted using a cross flow test cell. Membranes used for these tests were removed from water and immersed in isopropyl alcohol for 24 hours; they were then dried naturally to prevent pore collapse (Porter, 1990). At least three different rectangular membrane samples (0.13 meters x 0.09 meters) were cut from different membranes. The system was pressurized at 0.3 MPa. Each test was run for one hour and permeate flow was obtained using a graduated cylinder and a stop watch. Measurements were recorded each five minutes.

Based on the series resistance model, the permeate flux (J; [m^3/m^2.h]) was calculated using Equation (1). The clean membrane hydraulic resistance (R$_M$ [m^{-1}]) was calculated using Equation (2).

$$J = \frac{V}{A.t} \tag{1}$$

where V = permeate volume (m^3); A = membrane effective surface area (m^2); t=permeation time (s)

$$R_M = \frac{\Delta P}{\mu \times J} \tag{2}$$

where J = flux (m^3/m^2.s); ΔP = transmembrane pressure (Pa); μ = dynamic water viscosity (Pa.s)

Membrane Hydrophilicity

The membrane hydrophilicity was estimated by measuring the water contact angle (θ; [º]) of a sessile drop. Contact angle measurements were carried out according to the ISO-15989 standard method (International Standard, 2004).

The membranes used for these tests were removed from water and immersed in isopropyl alcohol for 24 hours and then dried naturally to prevent pore collapse. Two different rectangular membrane samples were cut from different membranes. At least fifteen tests for each type of membrane were made. Results were analyzed by the Median Test and Mann-Whitney Test.

Membrane Morphology Evaluation

Based on the Scanning Electron Microscopy (SEM) images, it was possible to determine the membrane pore sizes and distribution, using the ImageJ software. Membrane surface and cross-sectional images were obtained using a Quanta 600FEG Environmental Scanning Electron Microscope (ESEM), operated in the secondary electrons detection mode with a 10 kV accelerating voltage. All membrane samples were coated with a platinum layer.

RESULTS AND DISCUSSION
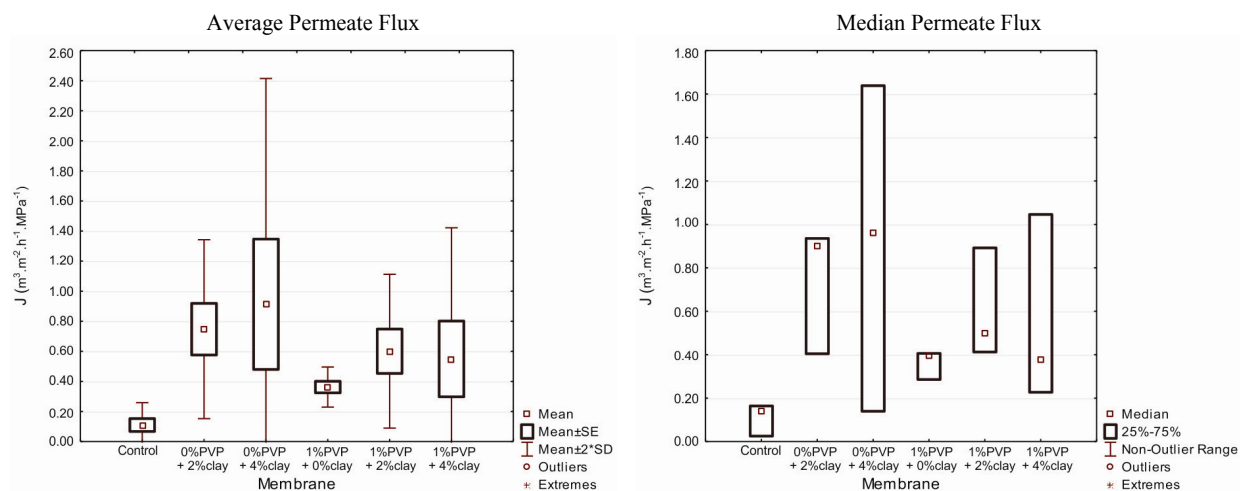
Membrane Performance Evaluation

Demineralized water flow tests were performed as a preliminary procedure to investigate the effect of clay nanoparticles and PVP addition on the PVDF membranes performance.

From Table 3 and Figure 1 it is possible to verify that the use of additives affects membrane permeability. The highest permeate flux (0.9130m^3.m^{-2}.h^{-1}.MPa^{-1}) was obtained for membranes cast with 0% PVP and 4% clay, showing an increase of 732% compared with the control membrane. The second highest (0.7473 m^3.m^{-2}.h^{-1}MPa^{-1}) was obtained for membranes cast with 0% PVP and 2% clay, with is 581% higher than the control membrane. However, the variance test, for a 5% significance level, between these two permeate flows, did not demonstrate that the variances are different. These results were expected because an improvement of pure water flux upon clay nanoparticle addition was also observed in previous studies (Mierzwa et al., 2013; Ma et al., 2012, Ghaemi et al., 2011; Monticelli et al., 2007).

The PVP addition also improved the pure water permeate flux. Comparing the (1% PVP + 0% clay) membrane permeability with the control membrane permeability the improvement was around 230%. This result agrees with previous reports that discuss the PVP influence on membrane morphology. According to Liu et al. (2011b), PVP acts more like a pore former in the modification of the PVDF membrane than as a hydrophilic additive because it is water soluble and can be removed during membrane preparation and operation. Furthermore, PVP addition affects the thermodynamics and kinetics of the casting process, changing membrane morphology, pore size and pore size distribution.

Table 3: Effect of additives on PVDF membrane performance.

Membrane	Average permeate flow $(m^3.m^{-2}.h^{-1})$	Average permeability		Median hydraulic resistance $(10^{+12}m^{-1})$
		$(m^3.m^{-2}.h^{-1}.MPa^{-1})$	$(L.m^{-2}h^{-1}.bar^{-1})$	
Control	0.032	0.1098	10.98	21.75
0% PVP + 2% clay	0.224	0.7473	74.73	3.47
0% PVP + 4% clay	0.274	0.9130	91.30	3.27
1% PVP + 0% clay	0.109	0.3623	36.23	7.94
1% PVP + 2% clay	0.180	0.6007	60.07	6.29
1% PVP + 4% clay	0.165	0.5494	54.94	8.25

Figure 1: Additive effect on PVDF membrane permeability.

According to the results presented in Table 3 and Figure 1, the combination of clay nanoparticles and PVP can improved the pure water permeate flux around 447% and 400%, respectively, for (1% PVP + 2% clay) and (1% PVP + 4% clay) membranes, compared to the control membrane. Nevertheless, membranes made with the combination of clay nanoparticles and PVP presented lower permeability compared with the membranes in which only clay nanoparticles were used. This behavior is related to the small PVP average molecular weight (10,000 g.mol^{-1}), which can lead to membranes with tight pores and reduced permeability. In order to confirm this hypothesis it is necessary to analyze and compare the membrane internal structure and also its separation capacity.

Table 3 also presents the results for membrane hydraulic resistance. The introduction of additives resulted in a lower hydraulic resistance. The hydraulic resistances for (0% PVP + 2% clay) and (0% PVP + 4% clay) membranes were about 6 to 7 times lower, respectively, when compared with control membrane. The other membranes had their hydraulic resistance reduced 3-fold relative to the control membrane. The variance test between the hydraulic

resistances of (0% PVP + 2% clay) and (0% PVP + 4% clay) membranes indicated that they were not different at the 5% significance level.

The median hydraulic resistance results agrees with the water permeate flux results; membranes that had the highest flux showed lower hydraulic resistance.

Membrane Hydrophilicity

Results for the contact angle measurements are presented in Table 4 and Figure 2. Because the contact angle measurements were very similar, the Median Test and Mann-Whitney Test were performed to better understand these results. Table 5 and Table 6 present the test results.

Table 5 shows that, in most cases (except for pairs control/0% PVP + 4% clay; 0% PVP + 2% clay /1% PVP + 0% clay; 0% PVP + 2% clay /1% PVP + 4% clay and 1% PVP + 0% clay /1% PVP + 4% clay) the contact angle results do not have the same median at the 95% confidence level. Table 6 indicates that the contact angle measurements do not come from populations with the same average at the 95% confidence level.

Table 4: Results of membrane hydrophilicity.

Membrane	Average Contact Angle (º)	Median Contact Angle (º)
Control	86.6	87.0
0% PVP + 2% clay	98.9	98.5
0% PVP + 4% clay	88.1	87.1
1% PVP + 0% clay	100.2	99.7
1% PVP + 2% clay	92.2	92.8
1% PVP + 4% clay	99.0	97.2
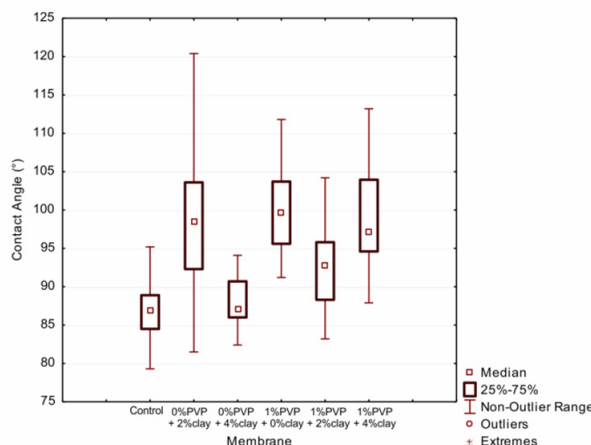
Figure 2: Median contact angles.

Table 5: Results of Median Test.

	0% PVP + 2% clay	0% PVP + 4% clay	1% PVP + 0% clay	1% PVP + 2% clay	1% PVP + 4% clay
Control	Non Homogeneous	Homogeneous	Non Homogeneous	Non Homogeneous	Non Homogeneous
0% PVP + 2% clay		Non Homogeneous	Homogeneous	Non Homogeneous	Homogeneous
0% PVP + 4% clay			Non Homogeneous	Non Homogeneous	Non Homogeneous
1% PVP + 0% clay				Non Homogeneous	Homogeneous
1% PVP + 2% clay					Non Homogeneous

Table 6: Results of Mann-Whitney Test.

	0% PVP + 2% clay	0% PVP + 4% clay	1% PVP + 0% clay	1% PVP + 2% clay	1% PVP + 4% clay
Control	Non Homogeneous	Non Homogeneous	Non Homogeneous	Non Homogeneous	Non Homogeneous
0% PVP + 2% clay		Non Homogeneous	Non Homogeneous	Non Homogeneous	Non Homogeneous
0% PVP + 4% clay			Non Homogeneous	Non Homogeneous	Non Homogeneous
1% PVP + 0% clay				Non Homogeneous	Non Homogeneous
1% PVP + 2% clay					Non Homogeneous

The contact angle results showed that clay nanoparticles and PVP addition affected membrane hydrophilicity. According to previous studies (Ghaemi *et al*., 2011; Anadão *et al*., 2010; Monticelli *et al*., 2007), it was expected that additives would decrease the contact angle and increase hydrophilicity, but the results have shown the opposite, since the control membrane had the lowest contact angle. Mierzwa *et al.* (2013) and Ma *et al.* (2012) demonstrated that

the nanoclay had little effect on the hydrophilicity of membranes.

Khulbe *et al.* (2003) concluded that the contact angle is related to the membrane surface roughness. The smaller membrane surface roughness, the smaller the contact angle. Therefore, the change in membrane contact angle using additives can be better explained by the changes in membrane roughness, as was pointed out by Mierzwa *et al.* (2013).

The permeability results and median contact angle results show that although additive introduction did not improve membrane hydrophilicity, it improved membrane permeability for pure water. These results are counter intuitive since higher permeability is associated with a more hydrophilic membrane. According to Mierzwa *et al.* (2012), contact angle is not a good indicator to predict permeability. Moreover, their studies suggest that membrane structure and pore size analysis provide better insights to understand the effects of additives on membrane performance.

Membrane Surface Morphology Evaluation

Membrane surface morphology can be analyzed in terms of pore size, pore distribution and porosity. These characteristics can be evaluated by surface SEM image analysis, as presented in Figure 3.

In order to understand the effect of additives on membrane morphological characteristics, the surface pore distributions and surface porosity were determined with SEM image analysis using the ImageJ software, as show in Figure 4. The surface pore size distributions are shown in Figure 5.
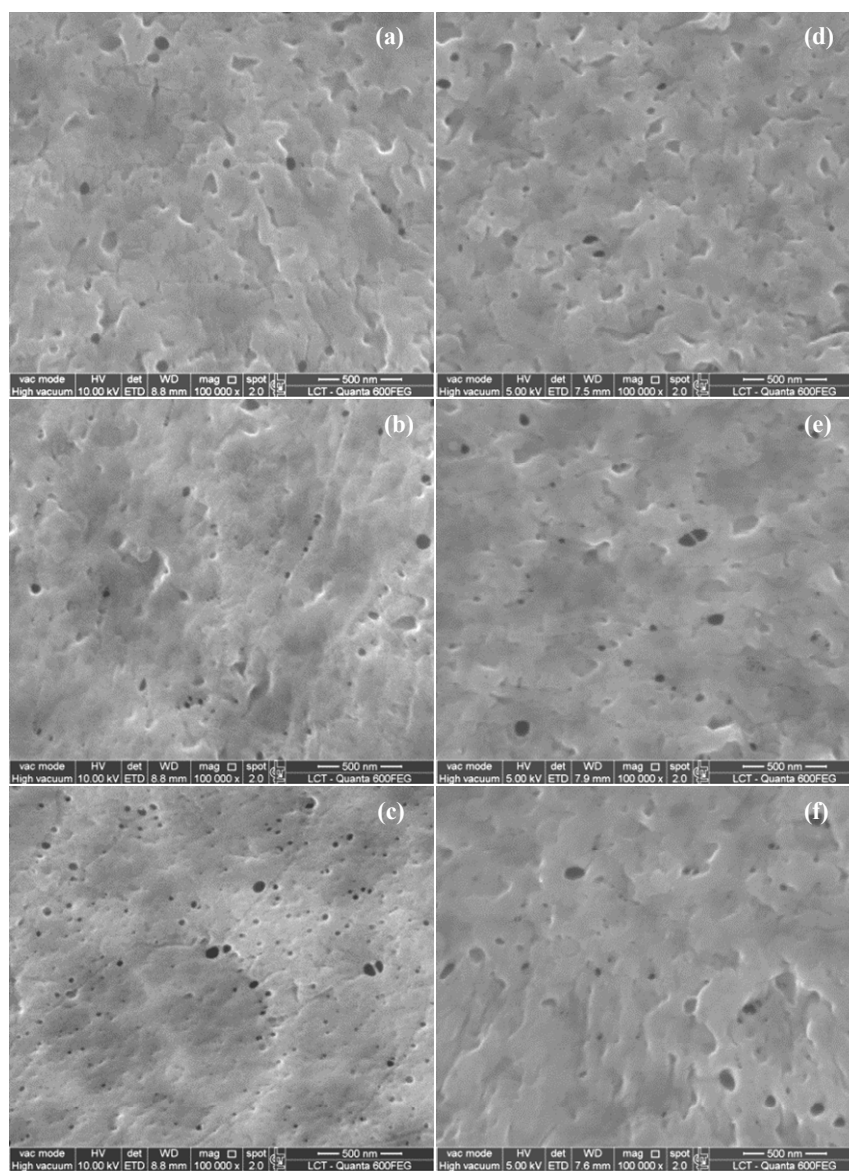
Figure 3: Membrane SEM surface images: (a) Control; (b) 0% PVP + 2% clay; (c) 0% PVP + 4% clay; (d) 1% PVP + 0% clay; (e) 1% PVP + 2% clay; (f) 1% PVP + 4% clay.
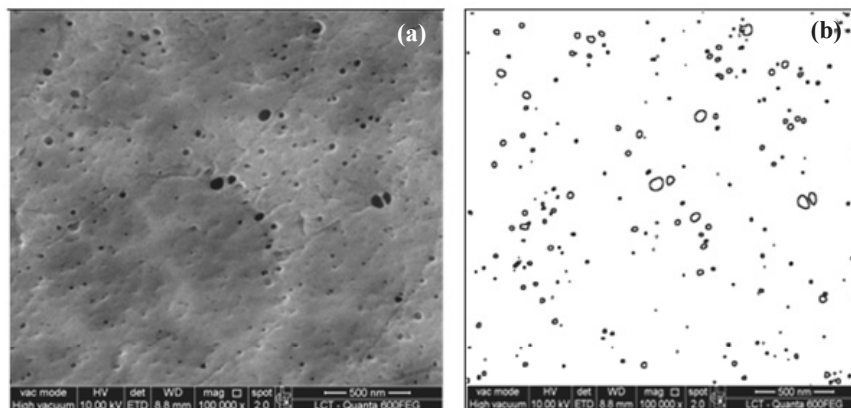
Figure 4: (0% PVP + 4% clay) membrane SEM surface image: (a) before manipulation; (b) after manipulation.
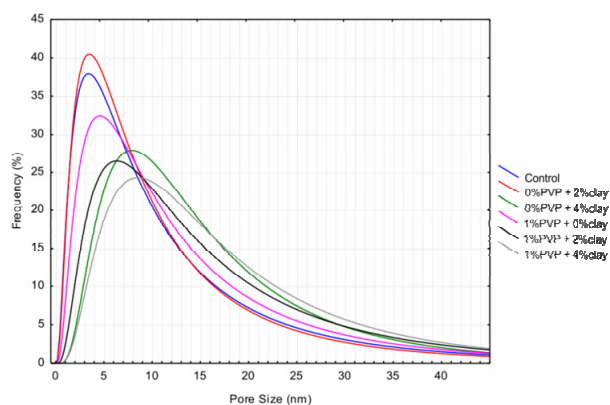
Figure 5: Membrane surface pore size distributions.

As observed in Figure 5, the (0% PVP + 4% clay) membrane, (1% PVP + 0% clay) membrane, (1% PVP + 2% clay) membrane and (1% PVP + 4% clay) membrane had their distribution curve peaks shifted to larger pore diameters and showed a larger base distribution when compared to the control membrane and the (0% PVP + 2% clay) membrane. The most frequent pore diameters found were: control membrane - 3.5 nm; (0% PVP + 2% clay) membrane - 3.5 nm; (0% PVP + 4% clay) membrane - 8nm; (1% PVP + 0% clay) membrane - 4.5 nm; (1% PVP + 2% clay) membrane - 6.5 nm; (1% PVP + 4% clay) membrane - 9nm.

It was observed that, in most cases, except for the (0% PVP + 2% clay) membrane, the addition of clay nanoparticles and PVP increased the pore diameter as well as broaden the pore size distribution. These results can justify the improvement in the composite membrane permeability, except for the (0% PVP + 2% clay) membrane, which presented a similar pore size distribution curve to the control membrane. This result indicates that the membrane internal morpho-

logy can significantly affect membrane performance, as was observed by Mierzwa *et al.* (2012).

Table 7 presents the results for surface porosity. It can be noted that the addition of nanoclay changed surface porosity. Surface porosity increased with increasing nanoclay concentrations, but in most cases nanoclay addition failed to improve the surface porosity compared to the control membrane. The PVP and nanoclay combination presented the lowest surface porosity, probably because of the low PVP molecular weight.

Table 7: Membrane surface porosity.

Membrane	Total Pore Area (nm^2)	Surface Porosity (%)
Control	26.160	0.47
0% PVP + 2% clay	25.357	0.45
0% PVP + 4% clay	53.564	0.95
1% PVP + 0% clay	36.290	0.65
1% PVP + 2% clay	17.013	0.30
1% PVP + 4% clay	20.514	0.37

Total membrane area: 5,606.068 nm^2

Despite the highest surface porosity and permeate flux presented by the (0% PVP + 4% clay) membrane, the surface porosity and surface pore size distribution results are not in such good agreement with the permeate test. This indicates that the internal pore morphology and structure have a major influence in the permeate flux performance.

Membrane Internal Morphology Evaluation

Membrane internal pore structure is an important morphology characteristic that can affect the membrane performance. The influence of additives on membrane internal morphology was evaluated by analysis of membrane cross-sectional SEM images. The cross-sectional SEM images for all cast membranes are presented in Figure 6.

From Figure 6 it can be observed that the type and concentration of additive affected the membrane pore structure. Nanoclay cast membrane morphology is characterized by a superficial layer with macropore, a bottom layer which has a sponge-like pore structure with micro-pores and an intermediate layer, with finger-like pores and micro-pores. This kind of structure was expected since previous studies (Hwang *et al*., 2011) showed similar structures of composite PVDF-Nanoclay membranes.

On the other hand, membranes with PVP had a
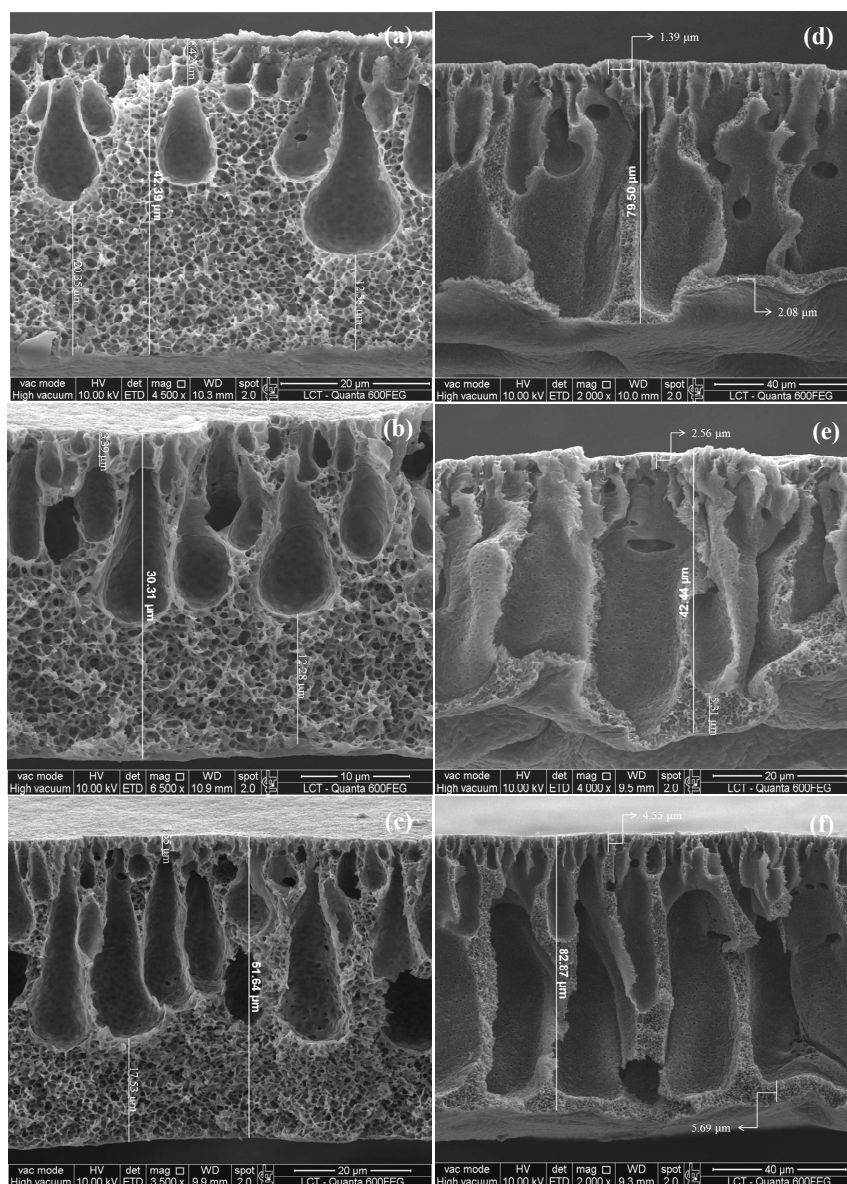
Figure 6: Membrane SEM cross-sectional images: (a) Control; (b) 0% PVP + 2% clay; (c) 0% PVP + 4% clay; (d) 1% PVP + 0% clay; (e) 1% PVP + 2% clay; (f) 1% PVP + 4% clay.

denser structure and also showed an intermediate layer characterized by macro-pores and longer and narrower finger-like pore structures. However, it shows an increasing number of finger-like pores. Besides, it can be observed that PVP introduction decreases the average pore size. These changes are proportional to the added PVP concentration added.

Membranes thickness characteristics are shown in Table 8.

It was expected that the final membrane had a 20% reduction in thickness. However, it can be observed in Table 8, the thickness reduction varies from 17% to 70%; the thicker membrane (1% PVP + 4% clay) had an estimated thickness of 82.87 μm and the thinner membrane (0% PVP + 2% clay) 30.31 μm. Membranes with only nanoclay (0% PVP + 2% clay membrane and 0% PVP + 4% clay membrane) showed the highest reduction in thickness compared to the membranes with nanoclay and PVP additions (1% PVP + 2% clay membrane and 1% PVP + 4% clay membrane).

Table 8: Membrane thickness characteristics.

Membrane	Thickness (μm)			% reduction in thickness[1]
	Total	Surface Layer	Bottom Layer	
Control	42.39	6.42	20.35	57.61
0% PVP + 2% clay	30.31	3.39	12.28	69.69
0% PVP + 4% clay	51.64	3.55	17.53	48.36
1% PVP + 0% clay	79.50	1.39	2.08	20.50
1% PVP + 2% clay	42.44	2.56	5.31	57.56
1% PVP + 4% clay	82.87	4.55	5.69	17.13

[1] Casting knife 100μm

Furthermore, the additives had different effects on the membrane internal layer thickness. The addition of nanoclay decreased the surface and bottom layer thicknesses, increased the intermediate layer thickness and also the number of finger-like pores. These changes are proportional to nanoclay concentration. The PVP and PVP-Nanoclay membranes had a reduction in bottom layer thickness compared to the nanoclay membranes.

Comparing the differences in internal membranes pore morphology and membranes performance, it can be noted that increasing the finger-like pore profile in the intermediated membrane layer improved permeability. Moreover, a less dense structure with a superficial layer with macro-pores, an intermediate layer with a finger-like pore structure and micro-pores and a bottom layer with sponge-like

pore structure and micro-pores provides an improvement in membrane permeability.

CONCLUSIONS

In this study, the influence of clay nanoparticles and PVP on the performance of PVDF membranes was evaluated.

The results of the performance evaluation tests suggest that the addition of clay nanoparticles and pore former (PVP) can improve the pure water permeate flux compared with a neat PVDF membrane. Moreover, the additions of only clay nanoparticles as an additive presented the best results for pure water permeate flux among all PVDF membranes compared. The use of 4%wt nanoclay concentration in the solution resulted in the membrane with the highest ultrapure water permeability.

The contact angle results indicate that additives increased the contact angle and decreased hydrophilicity, but, at the same time, the additives improved membrane permeability for pure water. This demonstrated that hydrophilicity is not responsible for the performance improvement.

Although the additives increased the distributions of pore diameter and the frequency of pores with higher diameter, composite membranes did not show better surface porosity results compared with the control membrane.

Furthermore, it was verified that the membrane surface porosity increased with increasing clay nanoparticle concentration. It was also observed that the morphology of this kind of membrane is characterized by a thin surface layer, with macro-pores, a thin bottom layer, which has a sponge structure with micro-pores and a thick intermediate layer, with finger-like pores and macro-pores. It was also verified that the addition of PVP promotes a denser morphology compared to membranes without it. The effect of clay nanoparticle addition on membrane performance seems to be associated with the changes in membrane morphology, increasing surface porosity and the extent of finger-like pores.

Laboratório de Caracterização Tecnológica (LCT), for the SEM analysis.

NOMENCLATURE

A	Membrane effective surface area	m^2
J	Permeate flux	$m^3/m^2.s$
R_M	Hydraulic resistance	m^{-1}
t	Permeation time	s
V	Permeate volume	m^3
ΔP	Transmembrane pressure	Pa

Greek Letters

θ	Contact angle	[º]
μ	Dynamic water viscosity	Pa.s

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