

Synthesis and Physical-Chemical Characterization of DEA-Crosslinked Poly(Vinyl Alcohol) Membranes

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Abstract : In this research, crosslinked PVA was impregnated with 0, 15 and 20% of diethanolamine so as to study the effect of the alkanolamine on the physical-chemical properties which are connected to the CO₂ separating process via membranes. Formaldehyde and a porous membrane of polysulfone were used as crosslinking agent and support, respectively. Membranes were characterized by FTIR, SEM-EDS, contact angle, water absorption and porosity measurements. The results suggest that although the water absorption in the bulk of polymer diminished when the percentage of diethanolamine increased, the surface hydrophilicity and appearance of the membranes were not appreciably affected due to this modification. A favorable balance of properties such as water uptake, the porosity and the superficial hydrophilicity were achieved using the crosslinking and synthesis conditions proposed in this paper, considering the positive effect of those characteristics in the permeability/selectivity of CO₂ through the membrane.

Keyword : crosslinked PVA, diethanolamine, CO₂ separating process, membranes, surface hydrophilicity.

Introduction

Pollution associated with emissions of carbon dioxide (CO₂) is one of the preeminent environmental issues [1,2]. The high level of CO₂ emission levels is arising from combustion of fossil fuel, accelerated increase in the energy consumption, population and industries, including cement and metal production, which have caused different kinds of devastating effects in particular the increase in global temperature with severe consequences on ecosystems, biodiversity and sea levels [3].

On account of the aforementioned scenario, the science, industry and governments have developed projects dealing with control greenhouse gases emissions in different approaches regarding reducing pollution through using non-fossil fuels, energy efficiency and separation techniques [3]. The technologies employed include the separation of carbon dioxide by cryogenic, absorption, adsorption and membranes, that can be effective to either capture or separate CO₂ originating from combustion of fossil fuels [4-6]. Although membrane separation technology has some merits including low energy demand and maintenance requirement alongside modular equipment and operational simplicity, it has not yet been considered commercially competitive [7, 8]. Polymer membrane processes are applicable to fuel cell [9-16], electrolytic removal of ions [17] and gas separation [2-4,6]. Although the gas selective polymeric membranes are a promising alternative to absorption processes and separation of carbon dioxide, there is a main drawback that is related to the fact that the production of membranes must be directed to the obtaining material properties as high selectivity and permeability, simultaneously [18].

There is an inverse relationship between selectivity and permeability [3, 19]; the permeability (P_i) is related with the transport flux of a gas (rate of gas permeation per unit area) in unit membrane thickness (l) per driving force that it is the pressure of component i between upstream and downstream of membrane side (cm^3 (STP).cm / [cm^2 .s.cm Hg]). Therefore, the selectivity (α_{AB}) is the ratio of permeances of component A y B (P_A/l and P_B/l) [20]. The permeance of gas i ($Q_i = P_i/l$) is represented as function of the material permeability with respect to gaseous component i and the effective membrane thickness l . High values of permeability are desired to be considered in the membrane processing. An increase in some parameters such as porosity can improve the permeation rates of gases through the membrane; however, this phenomenon leads to sacrifice the selectivity which would jeopardize its most important purpose.

The permeability of polymer membranes depends on a transport mechanism of the so-called solution-diffusion model [3, 19, 20]. In this model, is possible to identify three distinctive steps to describe the transportation process: firstly, gas is dissolved in the high-pressure feed side of the membrane; consequently, the diffusion of the gas into the polymer material takes place as a result of the movement through free volume between chains; Finally, the desorption of the gas from the low-pressure permeation side of the membrane occurs [3]. The preponderant factors during the diffusion stage are the amount of free volume [21] and the pressure difference. Free volume is the result of physical and chemical structural properties of the polymer and the pressure difference is directly related to the feed gas pressure, which usually is controlled by using compressors.

The facilitated transport membranes are used in the quest for reaching a satisfactory relationship between permeability and selectivity without high consumption of energy due to a compressive process and sweep gases [1, 7, 19]. In addition to the solution-diffusion model, this kind of membranes is governed by a facilitated diffusion mechanism with “carrier molecules” which react reversibly with the target CO_2 gas [19, 22]. The reaction between CO_2 and carriers result in a CO_2 -carrier complex on the feed side. If the carrier is a mobile molecule, the CO_2 -carrier complexes will move across the membrane, but if the complexes are formed with fixed carriers which have a limited mobility, CO_2 will react from a fixed carried to the next one closer by hopping mechanism in direction of concentration gradient [22]. The components which do not react with the carrier move through the membrane solely by the solution-diffusion mechanism [8, 19].

Compounds with amine groups such as alkanolamines can be used as carriers of CO_2 according with their parameters of reaction rate, absorption capacity and regeneration which are relevant in transport mechanism [1, 20, 23]. The alkanolamines have a favorable miscibility with the Poly(vinyl alcohol) (PVA), that was utilized in this study, this affinity is related to the attractive interactions between hydroxyl groups of PVA with amine groups of the carrier. PVA is a semi-crystalline polymer which has excellent physical properties, film-forming ability and formidable hydrophilicity [23], this last characteristic increases the free volume between polymeric chains causing the membrane swelling that enhance the selectivity in presence of water due to it is a physical solvent of CO_2 [20]. The crosslinking process can confer to the PVA film a higher thermal stability [23] while mechanical properties are improved with a microporous polysulfone (PSF) membrane as support, the polarity of this substrate allows the PVA-carrier solution to be extended homogeneously through the surface during the casting process.

Experimental

Materials

Poly(vinyl alcohol) (PVA) (99% hydrolyzed powder; $M_w = 77000$ - 79000) was purchased from J. T. Baker, microporous polysulfone (PSF) membrane (pore size= $0,45\mu$; diameter= 47mm) were obtained from Sigma-Aldrich, diethanolamine (DEA) ($M_w = 105,14$; $\rho = 1,09\text{kg/L}$), formaldehyde (37 wt% aqueous solution) and potassium hydroxide were supplied from Panreac.

Membrane synthesis

Facilitated transport membranes were synthesized by solution casting on a porous polysulfone support using the following methodology. An aqueous solution was prepared by dissolving 15g of PVA powder in 150 mL of water at 80°C for 24 hours in a sealed glass recipient. Subsequently, 18 mg of potassium hydroxide and $32\ \mu\text{L}$ of formaldehyde were added into the PVA solution for the crosslinking process, which took place at 80

°C during 24 hours. Finally, the temperature of the PVA crosslinked solution was reduced to 70°C so as to add the diethanolamine at the desired compositions blending for 6 hours. The entire above procedure was accomplished under vigorous and continuous stirring.

The crosslinked-PVA/diethanolamine solution was carefully poured into the petri dish, where the microporous support had been placed beforehand. After cooling at room temperature for 3 days for degassing the material, the membranes were allowed to completely be dried at 45°C in a vacuum oven.

Membrane characterization

Membranes synthesized in three composition (0, 15 and 20% of diethanolamine) were washed before the characterization with deionized water [24].

1. Water contact angle:

It was determined in order to establish the superficial characteristics of the membrane, based on the balance of the three phases (solid-liquid-gas) which interact when a drop of distilled water resting on a homogeneous and horizontal sample. The contact angle was measured between the line formed in the membrane-drop interface and the tangent line of the drop-air interface along the drop contour [25, 26]. The procedure was repeated 3 times and the average was calculated and reported.

2. Water uptake:

Samples with dimensions of 1cm x 1cm were weighed before being immersed in deionized water at room temperature. The samples were dried carefully with filter paper to remove excess water, then these were weighed and immersed for 24 and 48 hours further. Finally, water uptake was expressed in percentage according the following equation:

$$w(\%) = \frac{w_w - w_d}{w_d} \times 100 \quad (1)$$

Where w_d and w_w are the weight in g of membrane samples before and after immersion in water, respectively [23].

3. Porosity:

Samples with dimensions of 2cm x 2cm were weighed after being immersed for one hour in distilled water at room temperature and dried with filter paper to remove excess of water in the surface. The samples were placed in an oven at 80°C during 24 hours. Finally, the mass of the dried samples was determined. The weight of wet (Q_0) and dry (Q_1) samples were substituted in the following equation:

$$P(\%) = \frac{Q_0 - Q_1}{Ah} \times 1000 \quad (2)$$

Where P is the membrane porosity (%), A is the membrane surface area (cm²) and h is the membrane thickness (mm) [27].

4. Fourier transform infrared (FTIR) spectroscopy:

FTIR spectroscopy was used to identify changes in the chemical structure of membranes due to the crosslinked process and the presence of the alkanolamine DEA. FTIR spectra were collected at 4 cm⁻¹ resolution using 128 scans.

5. SEM-EDS:

Membrane surfaces were analyzed with scanning electron microscopy (SEM; JEOL JSM-6490). Additionally, the presence of the elements present in the samples was determined by energy dispersive spectroscopy (EDS).

Results and Discussion

1. Water contact angle

The superficial and bulk properties of polymers are related to each other, although they are generally quite different [28], the importance of surface properties is based on their functions during the first contact between feed gases and the membrane; in particular, a high wettability could improve the CO₂ absorption through the polymer considering its solubility in water. This affinity between the membrane and water can be established by contact angle measurement, which is dependent on the surface tension.

Surface tension or surface free energy is the result of the intermolecular forces [26], the van der Waals interaction and hydrogen bonds are the preeminent factors in polymers. Surfaces with a large number of polar groups such as OH groups have strong adhesive forces, good wettability and contact angle less than 90° [29]. For instance, PVA is a highly polar material due to the hydroxyl groups along the polymeric chain, which enables the formation of hydrogen bonds between those groups and water molecules. Therefore, the hydrophilicity of this polymer depends on the amount of available and accessible hydroxyl radicals.

It is widely known that crosslinking processes improve the mechanical and thermal properties of PVA membranes; however, this procedure promotes bounds between polymer chains and formaldehyde, limiting the available OH groups and the hydrophilicity. According to the above information, some authors have reported the increase of the contact angle in crosslinked polymers [30, 31]. In this work, all crosslinked PVA/diethanolamine membranes had a complete wettability the same as the non-crosslinked PVA, the drop was not detected in the surface of membrane either the contact angle. This results showed that a good combination of crosslinking conditions, without renouncing the desirable wettability, was achieved.

2. Water uptake

According to their structure and polarity, PVA can absorb a high amount of water; but in a crosslinked PVA, the polymer chains are organized in a stable three-dimension network which limit the accessibility to interactions regarding hydroxyl groups and water molecules. In spite of the reduction of water absorption, as a result of the crosslinking process, the necessity of this modification was evident due to the complete dissolution in water of non-crosslinked PVA membranes during the first 24 hours of immersion. The water uptake percentage as a function of DEA composition in the crosslinked PVA membranes are shown in Figure 1.

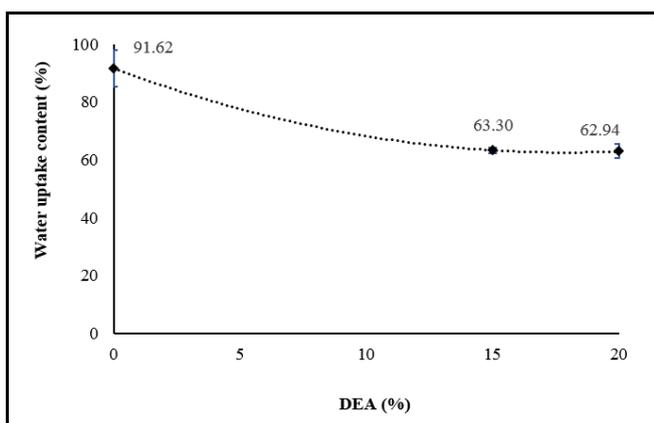


Figure 1. Water uptake of crosslinked PVA membranes based on the diethanolamine (DEA) content.

In Figure 1, it can be seen that water absorption in PVA membranes was decreased at high concentration of DEA due to the affinity of the hydroxyl groups of the polymer with the amine group of the secondary alkanolamine. The hydrogen bonds, between those species, limit the number of polar groups available in the membrane to interact with water molecules [23]. The water absorption was reduced slightly at high values of DEA. Figure 2 shows the potential hydrogen bonds formed between the crosslinked PVA with molecules of DEA and water.

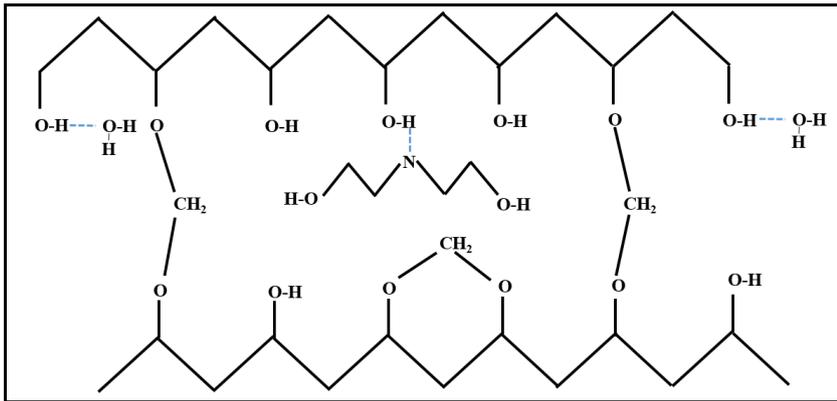


Figure 2. Crosslinked PVA with their potential interactions with molecules of water and diethanolamine.

3. Porosity

The crosslinked structure of PVA possesses strong bonds; therefore, a high concentration of DEA did not increase the void volume dramatically as long as the alkanolamine molecules can be positioned between the free spaces in the network. Figure 3 shows that DEA percentage did not affect the porosity of the material considerably.

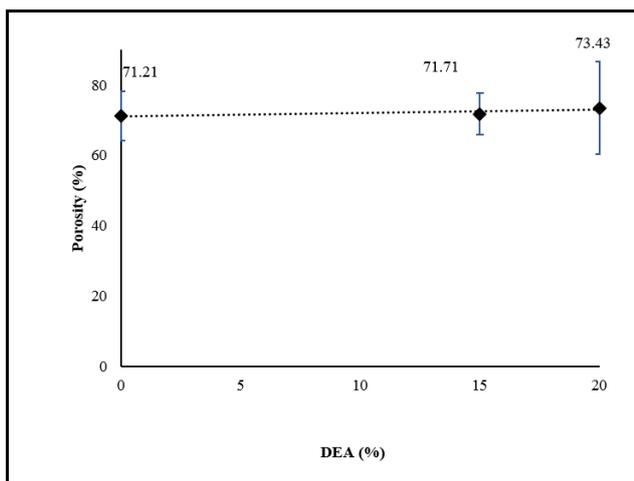


Figure 3. Porosity of crosslinked PVA membranes based on the diethanolamine (DEA) content.

4. Fourier transform infrared spectroscopy (FTIR)

FTIR spectra of crosslinked PVA membranes are shown in the Figure 4.

The peak at 1146 cm^{-1} is assigned to the symmetric C-O-C stretching, that is attributed to acetal linkage during the crosslinking process [7]. The intensity of this band was the same for all FTIR spectra, indicating that these membranes had similar degrees of crosslinking.

The -OH stretching band around 3300 cm^{-1} [8], shown in all curves, decreased at high values of DEA concentration. According with the similar crosslinking conditions in the membranes processing that were applied, this decreases can be due to a reduction of free hydroxyl groups by the hydrogen bonds formed by the polymer chain with DEA. Hence, the hydrophilicity and water absorption decreased, as shown in Figure 1.

The C-N stretching frequency was found at 1020 and 1340 cm^{-1} [18] exclusively in the membranes charged with DEA.

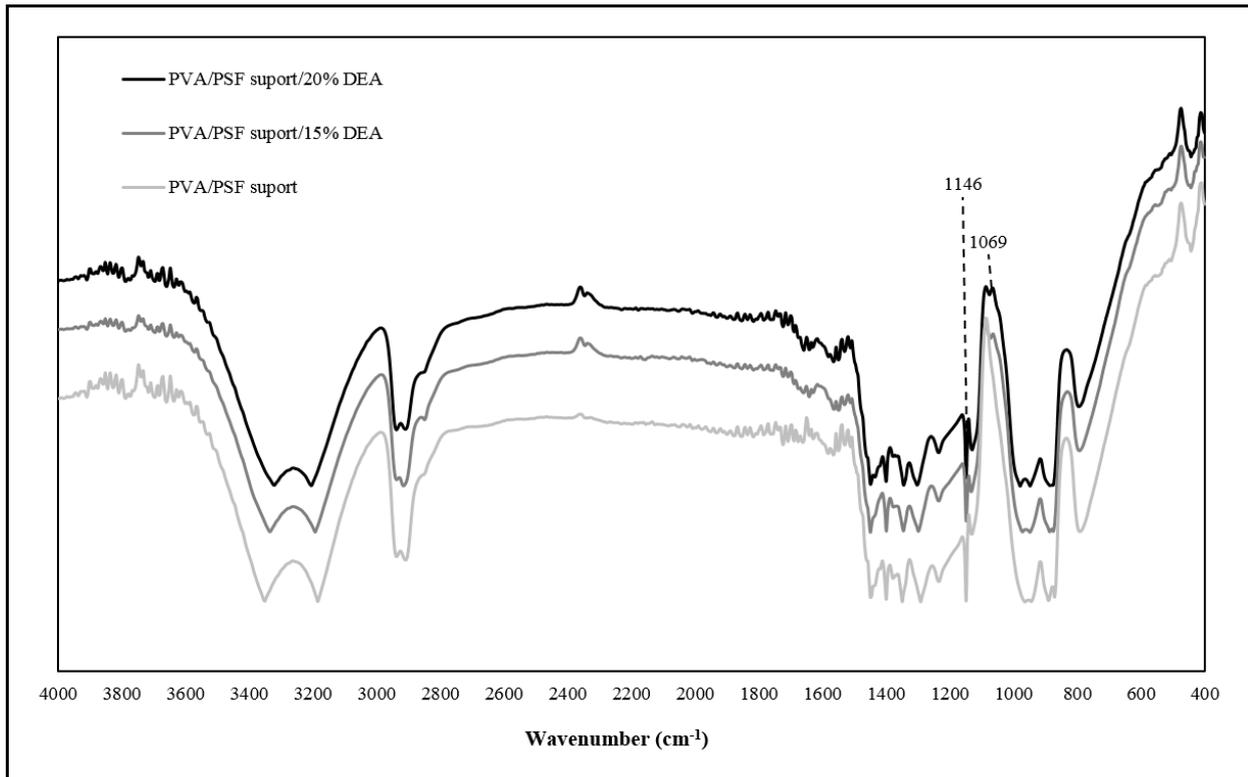
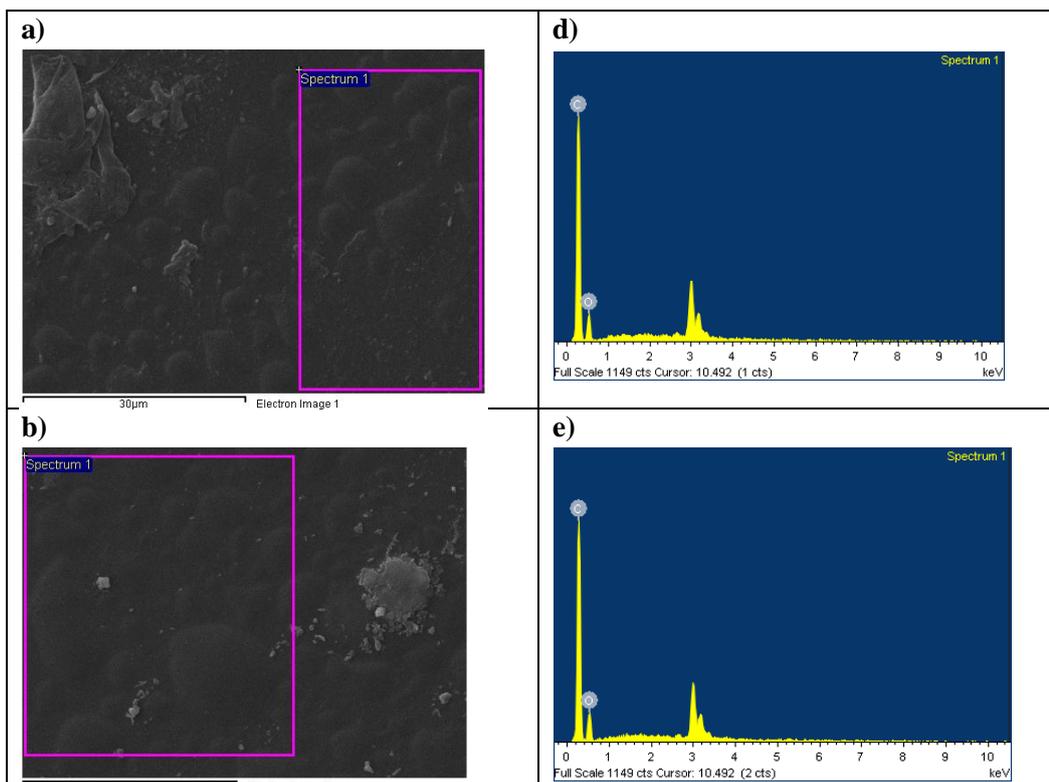


Figure 4. FTIR spectra of crosslinked PVA membranes based on the diethanolamine (DEA) content

5. SEM-EDS

SEM images of the crosslinked PVA membranes are shown in Figure 5 (a), (c) and (d). The surfaces are smooth with some heterogeneities, regardless of the DEA percentage. Nitrogen was not detected with EDS, for that reason Figure 5 (b), (d) and (e) are very similar.



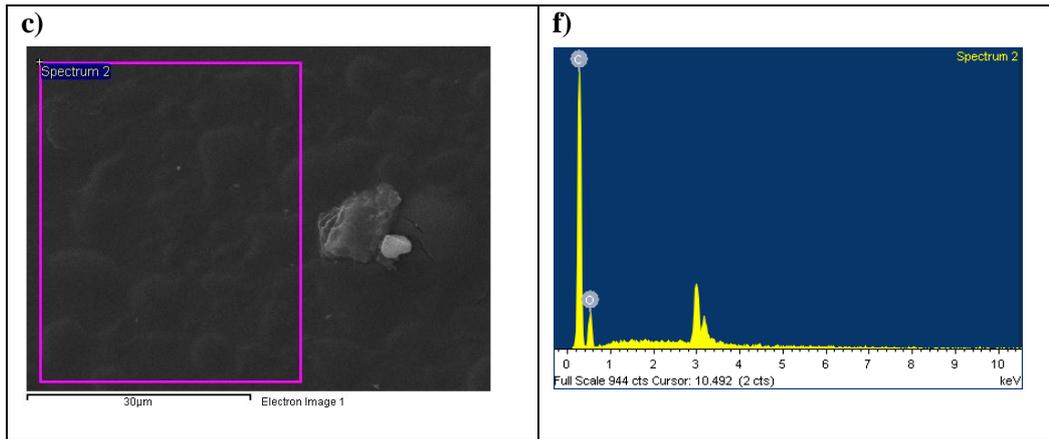
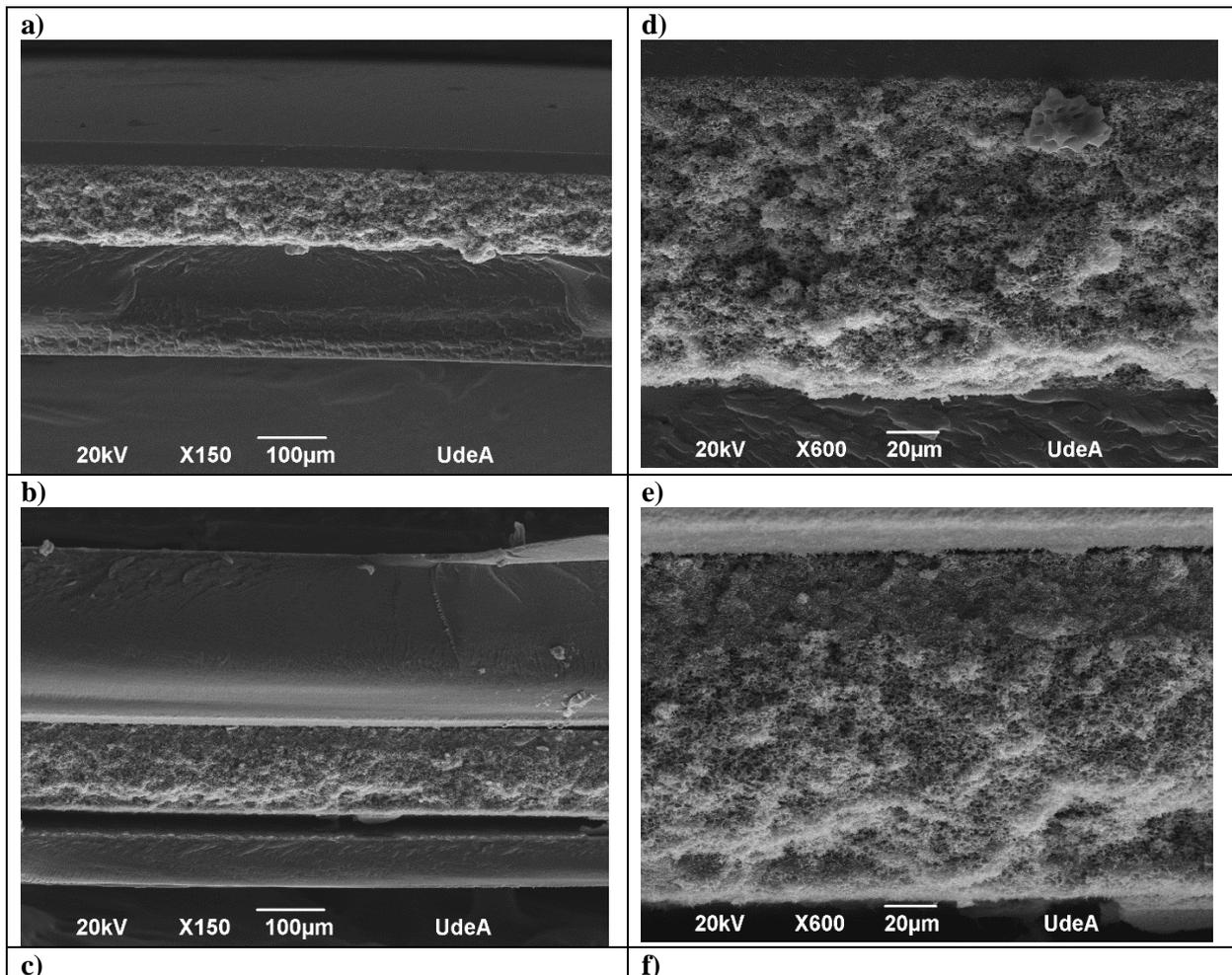


Figure 5. SEM images of (a) PVA, (b) PVA 15% DEA and (c) PVA 20%DEA. EDS of (d) PVA, (e) PVA 15% DEA and (f) PVA 20%DEA

As can be seen in Figure 6 (a), (b) and (c), two homogenous layers were formed on both sides of the crosslinked PVA membranes and macro-voids were not observed. The pores of PSF support were not completely filled by crosslinked PVA and crosslinked PVA with 15% DEA, as shown in Figure 6 (d) and (e) respectively. However, membranes with 20% DEA presented a partial permeation into the pores of PSF support.



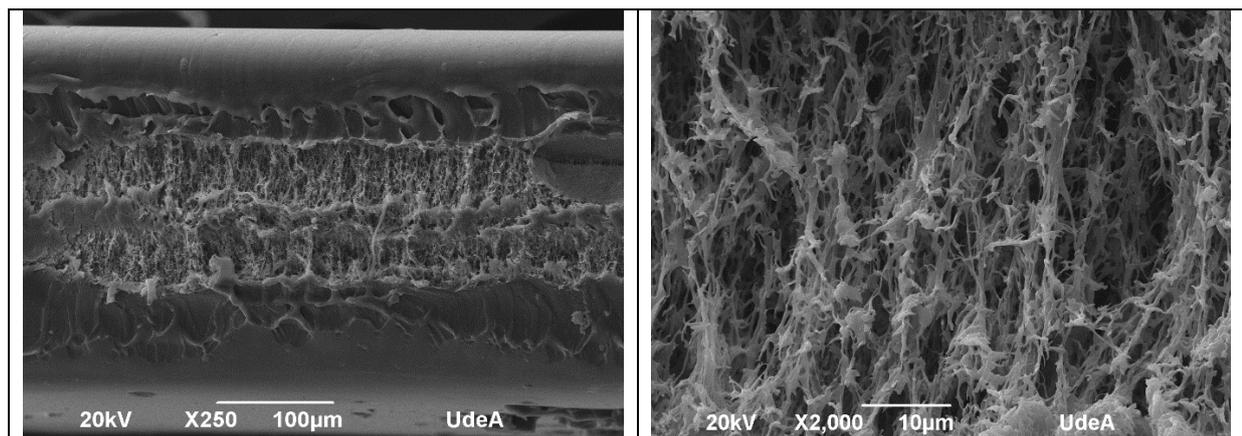


Figure 6. SEM cross-section images of (a) PVA, (b) PVA 15% DEA and (c) PVA 20%DEA. SEM cross-section of PSF support in (d) PVA, (e) PVA 15% DEA and (f) PVA 20%DEA membranes.

Conclusions

The content of DEA and the crosslinking process did not affect considerably the wettability of the PVA membranes. The crosslinked PVA membranes were insoluble in water. The percentage water uptake had a slight decrease at high DEA concentration. This phenomenon can be associated with the limitation of hydroxyl groups available in the polymer chain due to the hydrogen bonds between PVA and DEA. The reduction of free hydroxyl groups was confirmed by FTIR analysis. The percentage of DEA in PVA crosslinked membrane, did not affect the porosity dramatically and macro-void were not observed in the SEM images, which confers significant characteristics for membrane permeability.

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