

Modification of polyvinyl chloride (PVC) membrane for vacuum membrane distillation (VMD) application

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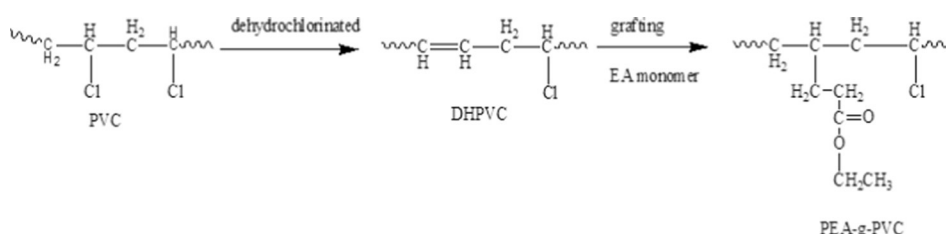
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HIGHLIGHTS

- Membrane modified by introduction of EA onto the PVC backbone, by free radical graft copolymerization
- Improved the porosity and contact angle of the modified membrane
- Highly porous membrane with largest pore size of 0.3 μm
- Permeate flux of the modified membrane was improved by about 15 times.
- Higher permeate flux of the modified membrane of about 37.5 ($\text{kg}/\text{m}^2 \text{ h}$)

GRAPHICAL ABSTRACT



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ABSTRACT

In the present work, hydrophobic modification of polyvinyl chloride (PVC) was performed with the introduction of ethyl acrylate (EA) monomer onto the polymer backbone, by free radical graft copolymerization. Membranes from polyvinyl chloride and grafted PVC solutions were prepared via immersion precipitation process for vacuum membrane distillation (VMD) application. The success of EA grafting onto PVC was confirmed by Fourier-transform infrared (FTIR) spectroscopy, and energy-dispersive X-ray spectroscopy (EDX). The membranes were characterized by scanning electron microscopy (SEM) analysis contact angle, pore size and porosity measurements. FTIR data showed that the PEA-g-PVC displayed new absorption peaks, indicating the introduction of the EA ester group on PVC. A significant difference between the spectrum of the PVC and PEA-g-PVC in the peak of chlorine and carbon was observed by using EDX analysis. The EA grafting onto PVC could affect the structural morphology of the PVC-g-PEA membranes, and increase the porosity, largest pore size and contact angle of the prepared membranes, whereas the membrane thickness is reduced. According to the results of VMD process on pure water, the permeate flux of the modified membrane was improved by about 15 times compared to the unmodified PVC membrane. The highest permeate flux of the modified membrane was about 37.5 $\text{kg}/\text{m}^2 \text{ h}$ at 60 °C of feed temperature and 2 mbar of vacuum pressure.

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1. Introduction

Nowadays, it is evident that the membrane engineering has been remarkably evolved and widely used on a large-scale because of the unique separation principles for plenty of applications, such as fresh water production [1,2], heavy metal removal [3,4], food industry [5–7], semiconductor [8], pharmaceutical [9] as well as power industries [10].

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For the purpose of obtaining the outstanding performance of the membrane for the applications mentioned above it is important to improve the membrane specifications, which can be done through several ways, including: optimum spinning conditions in membrane fabrication, addition of organic and/or inorganic additives in dope solution, surface graft polymerization, polymer–polymer blend, and polymer curing [11–17]. Among them, grafting process represents one of the most effective methods for modifying the properties of a polymer and therefore the membrane performance. However, two types of grafting could be employed: surface grafting and graft copolymerization (see Fig. 1).

Surface grafting is a method in which only the surface is modified, without changing the properties of the bulk. Generally, the effect found for surface parameters may be revealed both by radical chemical modifications of bulk polymer and by modification operated strictly at the surface level, without modifying the composition and properties of the bulk polymer. Surface graft polymerization has been used to modify membrane surfaces, using various surface activation methods including UV-irradiation [18,19], plasma treatment [20,21], ozone treatment [22,23], and chemical initiator [24,25] which can proceed via either free radical graft polymerization or living graft polymerization. Direct modification onto polymer surface results to the change of pore sizes and porosity and may lead to improve the performance of the polymeric membrane [26].

Graft copolymerization involves the reaction of a previously formed homopolymer or copolymer with fresh monomers [27] which are covalently bonded onto the polymer chains, and consequently conventional polymerization methods can be utilized. These techniques include chemical, radiation, photochemical, and plasma-induced methods and enzymatic grafting [13,28–30].

Plenty of polymers were used for the preparation of different membranes for specific applications. Among them poly(vinylchloride), exhibiting good thermal stability, chemical resistance, mechanical properties and excellent process ability, represents one of the world's major polymers in view of the large production amount and having a much diversified area of usage. Several synthetic methods for grafting

of PVC have been reported for different uses [31–35] such as grafting by ionic polymerization, polymer radical modification produced by γ -irradiation, atom transfer radical polymerization (ATRP) [36–38], and radical polymerization with chemical initiator [39,40]. Graft polymerization is also used in PVC modification to improve the performance of the polymer derivate and to exploit their application area [26].

In this work, the preparation of flat-sheet membranes produced by modification of PVC through free radical grafting polymerization with PEA for VMD application is reported for the first time. One of the main objectives of this work is substantiating our hypothesis that the grafted of EA on PVC results in an increase of hydrophobicity of the modified copolymer because of the nonpolar molecules and carbon chains of EA. The mass flux enhancement of the modified PEA-g-PVC membranes, the effect of the polymer concentration in the casting solution for both the pure and modified PVC on the morphology and performance of the membrane via VMD process were investigated. The prepared membranes were characterized using scanning electron microscopy (SEM), and contact angle, pore size, and porosity measurements. The grafted PVC was confirmed by Fourier-transform infrared (FTIR) spectroscopy, and energy-dispersive X-ray spectroscopy (EDX). After their characterization, the performance of both untreated and modified membranes was evaluated by VMD experiments.

2. Experimental work

2.1. Materials

PVC (MW = 65,000 g/mol) resin of an average degree of polymerization 1040 was obtained from Georgia Gulf Company (Georgia, USA). EA (BDH, England) was purified by distillation before using it. Sodium hydroxide (NaOH), methanol, benzoyl peroxide (BPO), cyclohexanone, and dimethylformamide (DMF) (Scharlan, Spain) were used during the radical grafting polymerization.

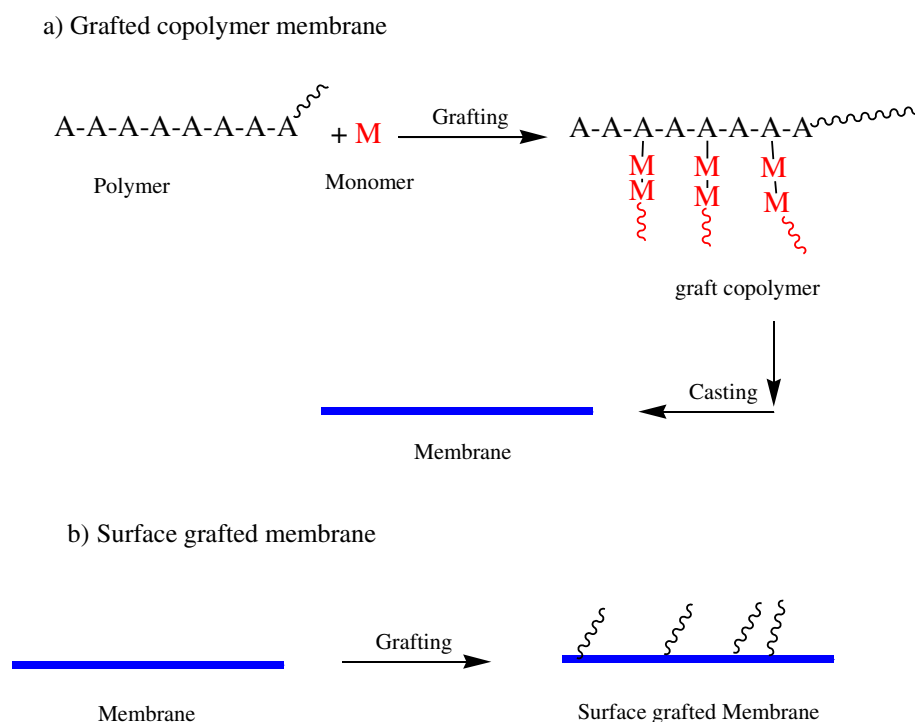
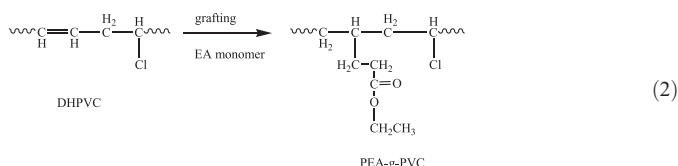
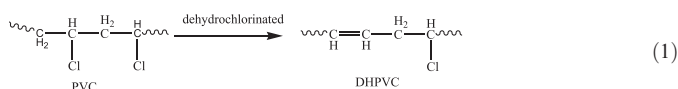


Fig. 1. a) Grafted copolymer membrane and b) surface grafted membrane.

2.2. Synthesis of copolymer

A weighed quantity of PVC and its 10 times of 10 wt.% NaOH solution were fed into a flask fitted with a reflux condenser. Dehydrochlorination proceeded (3 h) at 100 °C. The dehydrochlorinated product obtained in each case was washed with distilled water until removal of all traces of NaOH and then dried under vacuum. The reddish product is referred to as dehydrochlorinated PVC (DHPVC; see Eq. (1) given below). To prepare the grafted PVC, (11 g) DHPVC was dissolved in (150 ml) cyclohexanone; the solution was continuously stirred and heated up to desired temperature in an argon atmosphere. When the desired temperature was reached a known amount (13 g) of EA monomer containing a known quantity (1.68 g) of benzoyl peroxide (BPO) as initiator was added. The reaction was then carried out for predetermined time (1.5 h) to complete the grafting reaction. The mixture was then cooled and poured into excess well-stirred methanol. The precipitation polymer was filtered and washed for several times with methanol, then dried at 50 °C under vacuum overnight. The precipitate would be a mixture of poly(ethyl acrylate), PEA, homopolymer and grafted copolymer, PEA-g-PVC. PEA was removed by Soxhlet extraction using methanol. The remaining solid (PEA-g-PVC) was dried under vacuum and subsequently characterized (see Eq. (2)) [41,42].



The grafting parameters were evaluated from the mass of the sample before and after grafting. The percentage of graft yield was calculated according to the following equation:

$$\% \text{PEA in graft} = \text{Graft yield}(\%) = \frac{W1 - W2}{W2} \times 100 \quad (3)$$

where W1, W2 are the weights of graft copolymer, and DHPVC respectively.

2.3. Preparation of membrane

Polymeric casting solutions were prepared by mixing the copolymer, at two different concentrations (i.e., 14, and 18 wt.%) in DMF. The copolymer solution was stirred at a temperature of 55 °C until complete dissolution of the components was achieved. After 2 h of degassing, the dope solution was cast on a glass plate by using a 250 μm casting knife. Then, the nascent membrane was immersed in a non-solvent bath constituted by bidistilled water at 15 °C to achieve the complete solvent/non-solvent exchange.

The membranes were washed with plenty of hot water (60 °C) for three consecutive times to ensure the complete solvent removal. They were subsequently treated with a solution of 30 wt.% glycerol aqueous solution for 24 h to prevent the membrane pores from collapsing and finally dried at room temperature for 4 h. Prior to testing them in VMD experiments, membranes were washed with hot water (60 °C) for three consecutive times and then dried at 45 °C for at least 7 h in an oven.

2.4. Membrane characterization

2.4.1. Fourier-transform infrared (FTIR) spectroscopy

FTIR spectroscopy is a vibrational spectroscopy that records absorptions of IR light by chemical bonds in all molecules including polymers. Since different bonds absorb IR light at different wavelengths, FTIR spectroscopy is often referred to as fingerprint spectroscopy. As a consequence pure compounds have characteristic and unique FTIR spectra. Scanning was carried out from 4000 cm⁻¹ (2.5 μm) to 500 cm⁻¹ (20 μm) to confirm the formation of the graft copolymerization with FTIR-spectrophotometer (Shimadzu-IRTracer-100, Japan) at the Chemistry Department, Al-Mustansiriyah University, Iraq.

2.4.2. Scanning electron microscopy (SEM)

SEM is a common technique for analyzing the structure of the produced membranes. The membrane morphology was observed using a scanning electron microscope (ZEISS-EVO MA10).

The cross-sections of the flat sheet membranes were prepared by freeze fracturing in liquid nitrogen, to produce a clean, brittle fracture. The surfaces of the membranes were carefully cut in and fixed on a sample holder. After drying under vacuum, the samples were coated with a thin gold layer using a sputter apparatus (QUORUM Q150R-S) before observing them.

2.4.3. Energy-dispersive X-ray spectroscopy (EDX)

EDX is an analytical technique used for the elemental analysis or chemical characterization of the sample. The EDX analysis was performed by using a Quanta FENG 200 (FEI Company) microscope.

2.4.4. Contact angle

The hydrophobicity of the produced membrane was assessed by measurements of the water contact angle. In particular, the contact angle of the membranes was measured by using an optical instrument (CAM 100, Nordtest S.r.l., G-I, Italy). For each membrane, 6 analyses were performed both at air and glass side.

2.4.5. Thickness and porosity

The thickness of the membranes was measured using a digital micrometer (CARL MAHR micrometer-Germany) with a precision of ± 0.0001 mm at different locations of the membrane and the average value of five samples together with its standard deviation is taken into account.

Membrane porosity, defined as the volume of the pores divided by the total volume of the membrane, was evaluated after washing the membrane with distilled water in order to remove the glycerol from the membrane due to its effect on the porosity of the membrane, and dried for 4–5 h at 50 °C. These samples were weighed with a precision balance, then impregnated with kerosene for about 24 h and weighed again after wiping away superficial kerosene with filter paper [13]. Kerosene was chosen as wetting liquid instead of water due to the lower surface tension which makes it more pervasive within the pores of the membrane. The porosity of the membrane (ε) was estimated according to the following formula [43]:

$$\varepsilon (\%) = \left\{ \frac{(m_1 - m_2)/\rho_k}{[(m_1 - m_2)/\rho_k + m_2/\rho_p]} \right\} \times 100 \quad (4)$$

where m₁ is the weight of the wet membrane; m₂ is the weight of the dry membrane; ρ_k is the kerosene density (0.82 g/cm³); and ρ_p is the polymer density (1.35 g/cm³).

2.4.6. Bubble point and pore size

Bubble point and pore size of the flat sheet membranes prepared in this work were evaluated by liquid–gas displacement process, in which the non-reacting nitrogen displaces a wetting liquid from the membrane pores using a capillary flow porometer (Porous Materials Inc.,

USA). Measurements were carried out following the procedure described in literature [44].

Isopropanol (surface tension = 21.7 dyn/cm) was used as wetting liquid and data were processed by the software CapRep (Porous Materials Inc., USA). The membranes were analyzed with the wet up/dry up method, using the software CapWin (Porous Materials Inc., USA). The derived data were processed and exported in the excel format by the software CapRep (Porous Materials Inc., USA).

During a run, nitrogen gas is progressively compressed into the membrane. When the N_2 pressure defeats the capillary flow of the liquid inside the largest pore, the first nitrogen gas bubble is obtained. The compatible value of pressure is denoted as the bubble point of the membrane. Then, a further increase in the N_2 pressure until whole pores are vacuum gave the total pore size detection. N_2 pressure and the permeation flow rates through the membrane were measured. The two values of N_2 pressure are used to estimate the largest pore radius depending on the following equation:

$$r_p = \frac{2}{\Delta P} (\sigma \cos \phi) \quad (5)$$

where r_p is pore radius; σ is the surface tension of the liquid; and ϕ is the contact angle between liquid and membrane surface. The membrane is completely wetted by the isopropanol, therefore, $\phi = 0$, then, $\cos \phi$ is expected to be 1.

2.5. VMD process

The VMD experiments were carried out using the laboratory system shown in Fig. 2. The feed solution was heated outside the module, and then sent in contact with one side of the membrane, while vacuum was applied at the other side, where a trap immersed in liquid nitrogen was used to condense and collect the vapor. The liquid permeate was, then, measured by a balance. The effective membrane area of the module was 7.54 cm². VMD tests were performed using double distilled water as feed at different temperatures and vacuum pressures and at a fixed feed flow rate of 40 L/h. The performance of all membranes was

compared by operating the VMD system under the same conditions. All VMD experiments were repeated at least two times in order to check the reproducibility of the measurements. The distillate flux, J (kg/m² h), was calculated according to the following equation [45,46]:

$$J = \frac{M}{A \cdot t} \quad (5)$$

where M is the mass of permeate; A is the active membrane surface; t is the time interval.

3. Results and discussion

3.1. Confirmation of grafting by FTIR

FTIR spectra of neat PVC and PEA-g-PVC (yield rate: Gp 20%) grafted copolymers are illustrated in Fig. 3. It can be observed that the grafted copolymer displayed new absorption peaks at 1732 cm⁻¹, 1101 cm⁻¹, and 1022 cm⁻¹. These peaks indicate the introduction of the ester group of EA from PEA grafted onto PVC backbone.

FTIR peaks at 2976, 2916, 2941 cm⁻¹ were belong to aliphatic C–H stretching vibration; and 1732 cm⁻¹ belongs to the C=O ester stretching vibration, corresponding to the carbonyl stretching from the acrylate groups [47]. In Fig. 3, the peaks at 1425, 1352, and 1329 cm⁻¹ belong to aliphatic CH₃–CH₂ deformation vibration; while the peak at 1253 cm⁻¹ represents the C–C stretching vibration; the peaks at 1022 cm⁻¹ belong to the C–O–C single bond stretching vibration of the ester group; the single bond deformation vibration of the ester group C–O–C appears at 962 and 856 cm⁻¹, and C–Cl stretching vibration peaks appear at 623 cm⁻¹, and 693 cm⁻¹ became smaller after the grafting. Therefore, all these peaks are a good indication of successful grafting of EA onto PVC.

3.2. Morphology examination by EDX

Fig. 4a and b show the EDX spectrum of the PVC and PEA-g-PVC membranes, respectively, recorded with the “light element” detector

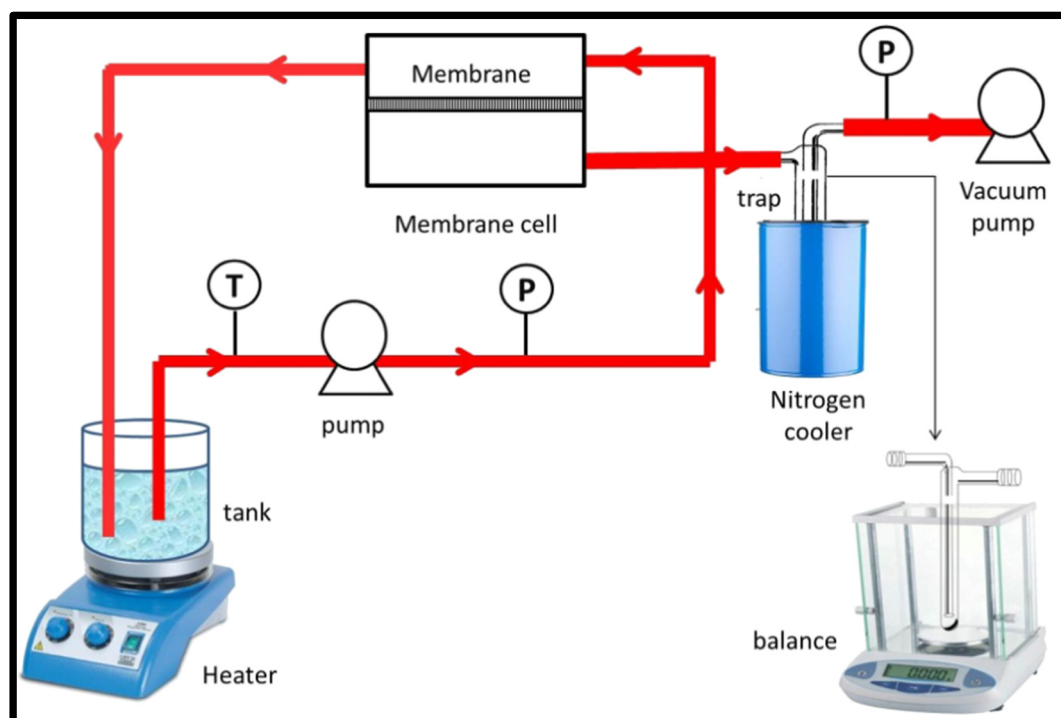


Fig. 2. Schematic diagram of the vacuum membrane distillation (VMD) experimental rig.

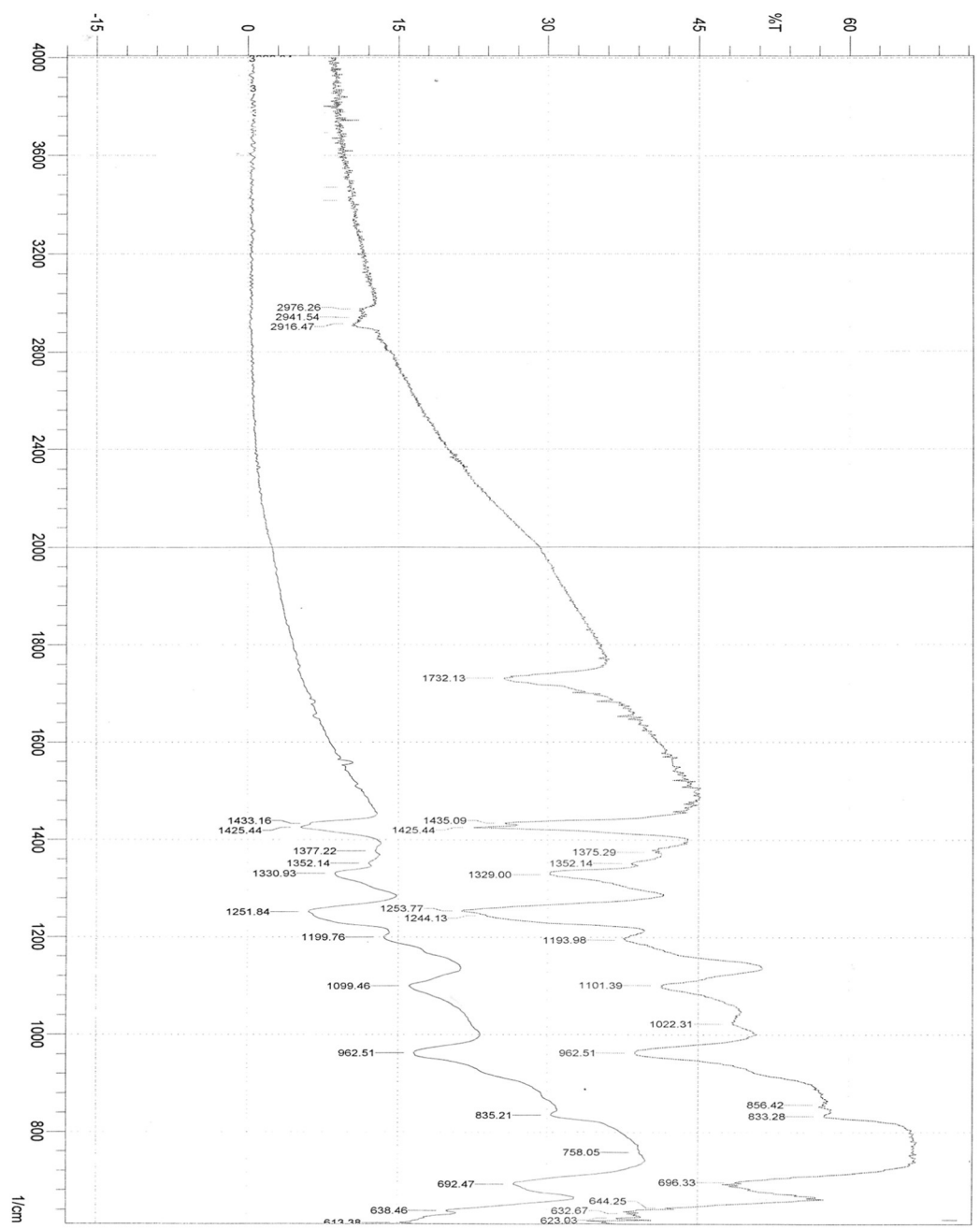


Fig. 3. FTIR spectra of PVC-g-EA copolymer.

at 10 kV. It has been noticed that there is a significant difference between the spectrum of the PVC and PEA-g-PVC samples in the peaks of chlorine and carbon. The comparison between these spectra became evident when the carbon peak had been increased, and at the same time a small peak attributable to the oxygen atoms increased, too, whereas, the chloride one had been decreased. Therefore, it has been confirmed that the decreasing in the chloride percentage is due to dehydrochlorination, while both the increasing of the percentage of carbon and the appearance of the oxygen demonstrates the existence of the ester group which belongs to the EA monomer. Moreover, such differences in the peak height confirm the percentage of grafting (i.e., 20%) calculated according to Eq. (3), while according to Table 1 which illustrated the weight percentage of the elements measured by EDX it was found that the reduction in weight percentage of Cl in PEA-g-PVC copolymer is 19.7%.

3.3. Morphology examination by SEM

Fig. 5 shows the SEM pictures of the top surface of the unmodified PVC membranes prepared starting from different PVC concentrations (i.e., 14, and 18 wt.%). It can be observed from Fig. 5a that the membrane prepared from 18 wt.% presented a dense structure with no pores on the surface. In Fig. 5b, the SEM picture of the top surface of the membrane, prepared from 14 wt.% PVC, presented rough surface with some pores dispersed on the surface. This phenomenon is due to the higher PVC content at the film interface, which results in less pores on the top layer of the membrane, and this behavior is also reported in the literature [46,48–50].

The SEM pictures related to the top surface of the membranes prepared with the PVC modified by free radical grafting polymerization with PEA [PEA-g-PVC copolymer (Gp 20%)] are illustrated in Fig. 6. It

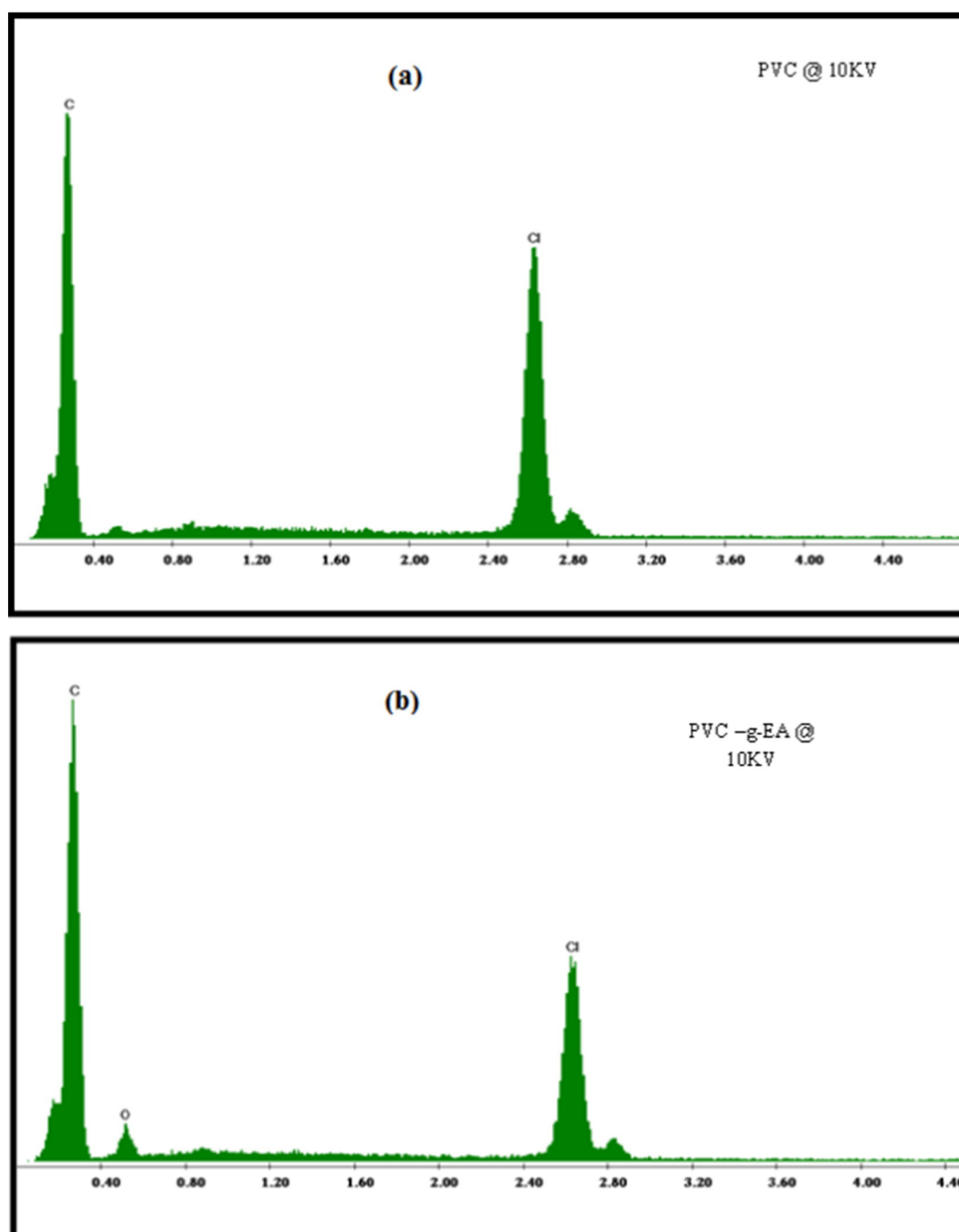


Fig. 4. Energy-dispersive X-ray spectroscopy (EDX) of: (a) PVC and (b) PVC-g-EA at 10 kV.

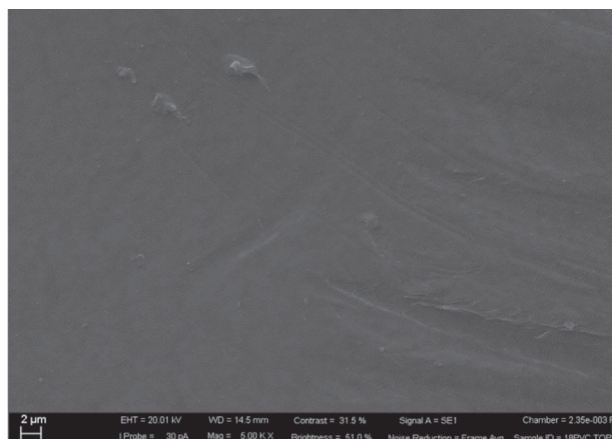
can be observed from Fig. 6a that the membrane prepared from modified 18 wt.% PVC presented rough structure with few pores on the top surface of the membrane. Similar structure was observed for the samples obtained with the modified 14 wt.% PVC, which showed many

Table 1

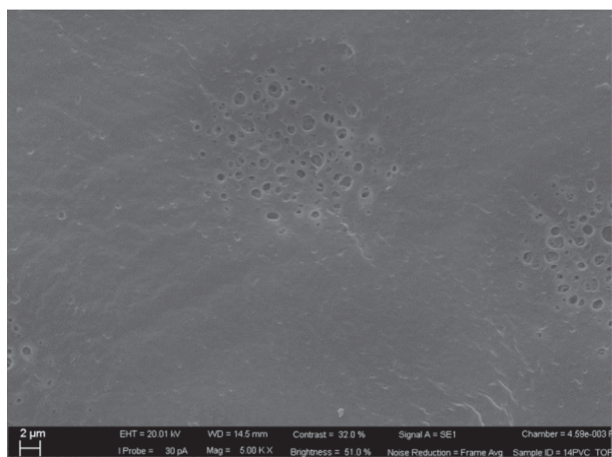
Weight and atomic percentages of elements in PVC and PEA-g-PVC of the EDX test.

| Element | PVC | | PEA-g-PVC | |
|---------|-------|----------|-----------|----------|
| | Wt.% | Atomic % | Wt.% | Atomic % |
| C | 74.13 | 89.43 | 76.33 | 89.22 |
| O | – | – | 2.92 | 2.56 |
| Cl | 25.86 | 10.57 | 20.76 | 8.22 |

pores sparse on the top surface of the membrane as it can be seen in Fig. 6b. The differences in the surface morphology for the membranes prepared from pristine and modified PVC with PEA is attributed to the viscosity of the casting solutions. The viscosity of casting solutions prepared with the unmodified PVC was higher than those obtained with the grafted polymer having the same concentration as shown in Fig. 7. This was probably related to the presence of PEA branches on PVC backbone [51], which affect the density of the polymer and consequently the viscosity of the dope solution. The increasing/decreasing of the polymer density depends on the number and the length of the branches. Moreover, while increasing the polymer content, the viscosity of the casting solution increases, which in turn leads to an increase of the polymer concentration at the film interface between the neat PVC and the

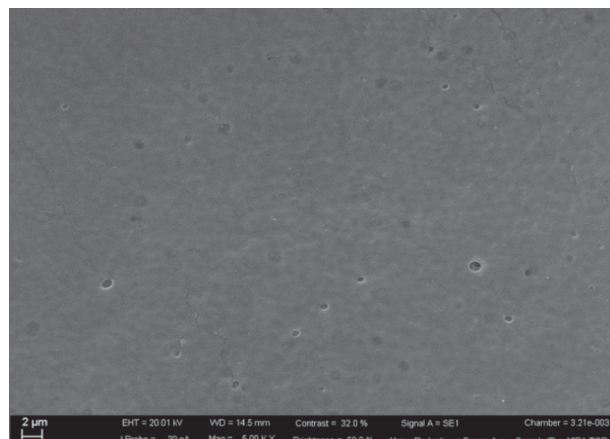


(a)

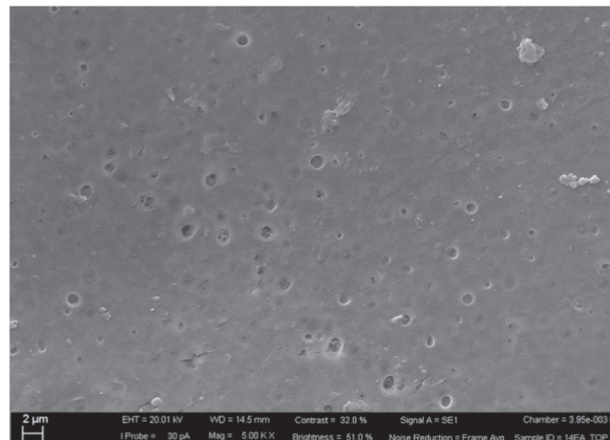


(b)

Fig. 5. SEM images of neat PVC top membrane surfaces: (a) 18% and (b) 14%.



(a)



(b)

Fig. 6. SEM images of PVC-g-EA top membrane surfaces: (a) 18 wt.% and (b) 14 wt.%.

solvent, promoting the formation of thick, dense membranes and at the same time, suppressing the pore formation.

The smallest PEA-g-PVC concentration led to a lower membrane thickness and promoted the pore formation on the top layer and the increase in the pore size [27,52,53]. This change in structural morphology of the membranes prepared from PVC modified with PEA confirmed our objective that the grafted PVC by PEA drives to an increase of the mutual affinity of the modified PVC with DMF. The affinity between the polymer and solvent increases, as the difference between the solubility parameters δ_s and δ_p of the solvent and polymer respectively becomes smaller. Therefore, the solubility difference between DMF-PVC is higher than that of DMF-PEA.

The SEM pictures of the cross sections of the membranes prepared from PVC and modified PEA-g-PVC are presented in Fig. 8. It can be observed that the cross section of the membrane prepared from neat PVC was composed of three layers, two sponge-like structure layers appear near the top and bottom surfaces, whereas macro-void structures appear in the middle of the cross section (Fig. 8a). In Fig. 8b, it could be observed that the cross section structure of the modified 14 wt.% PVC that presented an asymmetric structure, consisting of tear-voids distributed inside a sponge-like structure sits toward the bottom surface. Moreover, finger-like structure appears near the top surface of the membrane, whereas, the cross section of the modified 18 wt.% PVC presented finger-like structure and some sponge-like parts dispersed between the macrovoids as shown in Fig. 8c. Also, it is worth to mention here that an observation from Fig. 8c can be expected, where there is a beginning change of cross section structure from finger to sponge-like structure in modified PVC membrane structure.

Based on these results a speculation on which factors develop the porous membrane formation is reported.

The final membrane morphology, according to Strathmann et al. [54], and other authors [55], can be related to the rate of precipitation. If the rate of precipitation is high, the formation of finger-like cavities is favored. By contrast, lowering the demixing rate led in denser, more porous membranes. The formation of the non-porous dense skin layer can be related to the delayed onset of the liquid–liquid demixing [56]. In our case, the precipitation is expected to occur very fast in water bath and the formation of the non-porous dense skin layer can be related to the instant-demixing.

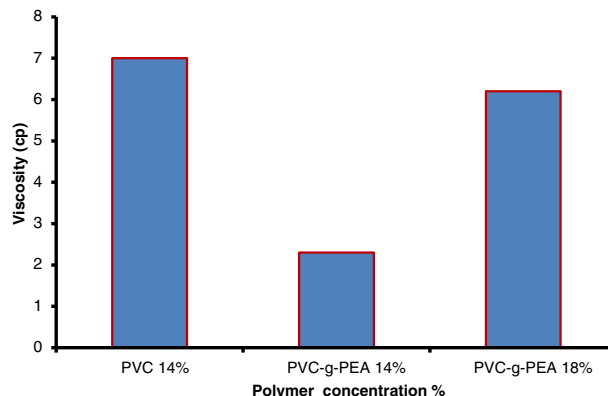


Fig. 7. Viscosity of the casting solutions prepared from neat and modified PVC.

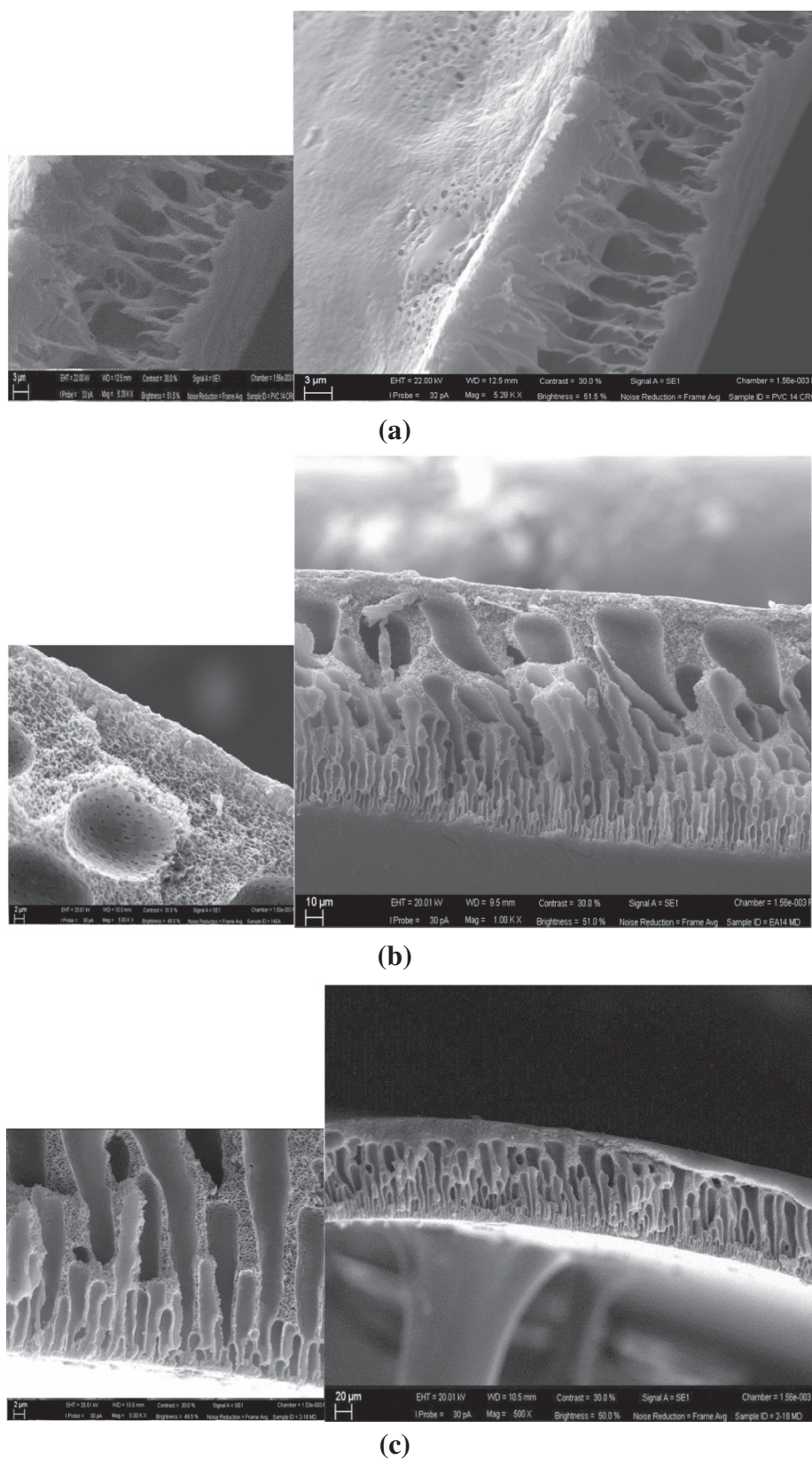


Fig. 8. SEM images of membrane cross sections: (a) 14% neat PVC, (b) 14% PVC-g-PEA, and (c) 18% PVC-g-PEA.

During the phase inversion process, the polymer precipitation rate decreases from the top to the bottom surface of the nascent film, resulting in asymmetric structure (finger-like on the top and sponge-type on the bottom side because of the delayed separation time).

The polymer also plays a crucial role in affecting the membrane morphology. Increasing its content in the dope solution corresponds to a higher fraction of polymer and a high solution viscosity, leading to a decrease in the pore size and the porosity of the membrane.

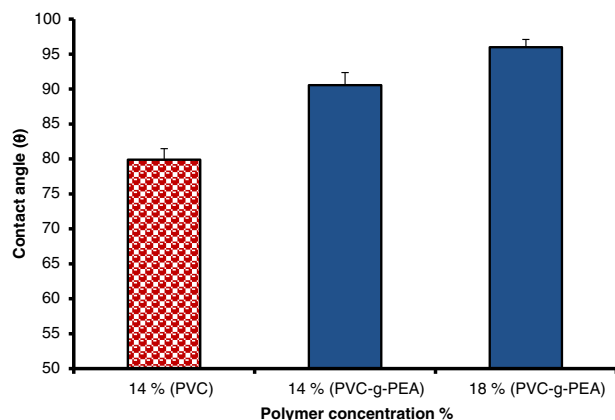


Fig. 9. The effect of polymer concentration on membrane hydrophobicity (contact angle); for PVC-g-PEA and neat PVC.

In this work, the exchange between DMF and water was fast due to their strong affinity and high miscibility, as demonstrated by the predominantly finger-like form. However, the increasing of the polymer concentration in the casting solution limited the speed of the non-solvent diffusion across the nascent membrane, which in turn leads to give a combination of sponge and finger-like structures [46,57].

3.4. Contact angle measurements

In contact angle measurement all membranes were screened by using bidistilled water, in order to evaluate their hydrophobic character and, hence, their applicability in VMD process. Fig. 9 shows the water contact angle values of the 14 wt.% PVC membrane and two different modified PEA-g-PVC membranes. It can be noticed that the membrane prepared from 14 wt.% PVC has lower water contact angle of $79 \pm 1^\circ$ than that of the modified PEA-g-PVC membranes. Furthermore, it is noticed that as the polymer concentration increased in the casting solution, the water contact angle increased and the obtained values were $90.5 \pm 1^\circ$ and $96 \pm 1^\circ$ for 14 and 18 wt.%, respectively. These results confirm our hypothesis that the grafted of EA on PVC leads to increase the hydrophobicity of the modified membranes. Hydrophobic PEA is a nonpolar molecule and has chain of carbons; therefore, it does not interact with water molecules. Since the strength of hydrophobic interactions depends on the number of carbon atoms in the hydrophobic polymer and the shape of the branched chain.

Moreover, increasing water contact angle with increasing of polymer content is essentially due to the membrane surface morphology, which in turn provides high hydrophobic property of membrane. Also, increasing polymer concentration helps to decrease pore size of the membrane and results to higher mass flux resistance against water vapor to penetrate throughout the membranes and similar behavior was found in the literature [16,50,58–60].

3.5. Porosity, pore size and thickness of membranes

Membrane porosity is denoted as the void fraction of the membrane and in our opinion this parameter is one of the most important factors affecting the efficiency of the performance of the membrane especially for MD application. In general, MD membrane porosity is reported to be between 35% and 93% [61,62]. Anywise, higher is the porosity value lead to depress the resistance toward the water vapors through the membrane. Fig. 10 shows the porosity of the membranes prepared from unmodified PVC and modified PEA-g-PVC at two different PVC concentrations. It can be seen that the porosity of the membrane prepared from 14 wt.% PVC improved from about 80.6 to about 83.7%

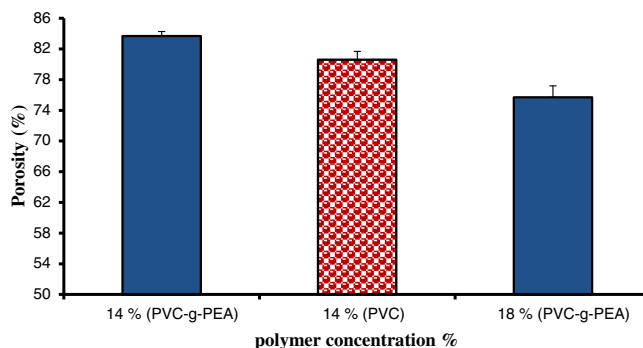


Fig. 10. Effect of polymer concentration for the neat and modified PVC membranes on porosity of the membranes.

after modification of the PVC at the same concentration with PEA (14 wt.% PEA-g-PVC). This phenomenon is due to the low viscosity of the casting solution prepared from modified polymer compared to that of 14 wt.% PVC, because of the effect of PEA branches on PVC backbone. Moreover, increasing of PVC concentration in the grafted polymer with PEA, such as 14 and 18 wt.%, results to high decrease in the porosity of the membrane. In particular, the porosity of the membrane prepared with 14 wt.% is about 83.68%, whereas, the porosity of the membrane prepared from 18 wt.% corresponds to 75.70%. This predictable result is attributed to the increase in the viscosity of the casting solution with the increase of PVC concentration. In this case slowness exchange rate between solvent and non-solvent during the precipitation process of the polymer is obtained. Therefore, higher polymer concentration is being realized at the non-solvent-polymer solution interface and conducted to the formation of membrane with lower porosity. Generally, it was reported that the porosity of the membrane reduced with the increase in polymer concentration of the casting solution [63,64].

The most interesting factor that affected the membrane performance in MD application especially for VMD configuration is the pore size of the membrane. In general, the pores in the prepared membranes do not have similar size at the surface but appear with different sizes. Therefore, in MD the pores should be large enough to expedite the desired mass flux and in the same time the prevention of liquid diffusion inside the membrane pores under the VMD operating conditions should be taken into account [65]. Accordingly, in this work the largest pore size is taken into consideration for the determination of the VMD mass flux performance as illustrated in Fig. 11.

In Fig. 11, it is shown that the largest pore size of the modified PVC membrane decreases as the polymer concentration increases from 14 wt.% to 18 wt.%. Also it can be seen from Fig. 11 that the largest pore size of the 14 wt.% PVC membrane is smaller than the 14 wt.%

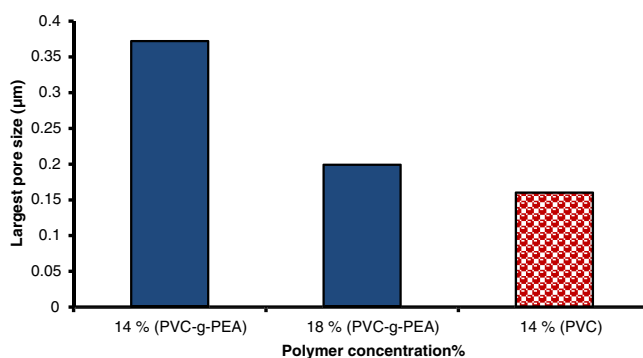


Fig. 11. Effect of polymer concentration for the neat and modified PVC membranes on largest pore size of the membranes.

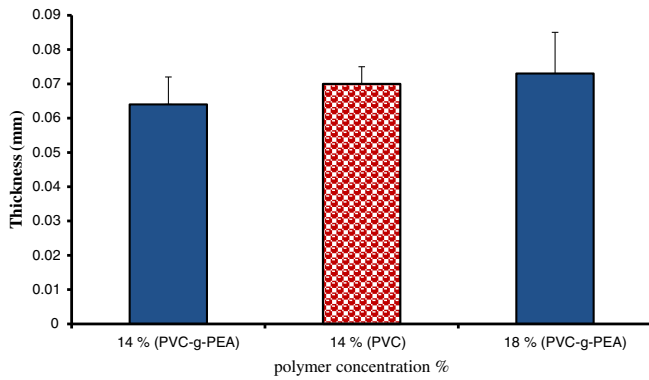


Fig. 12. Effect of polymer concentration for the neat and modified PVC membranes on thickness of the membranes.

modified membrane. In general, as the polymer concentration in casting solution increases the pore size of the prepared membrane decreases. This behavior is attributed to the closed membrane structure during membrane formation with increasing of polymer concentration in casting solution. It is evident that increasing polymer concentration increases viscosity of the casting solution, which in turn delays the penetration process of non-solvent to the polymer solution during the formation of the membrane, and therefore, lower pore size is obtained, and similar behavior has been already reported in literature [48,66–69].

The effect of different polymer concentrations for unmodified and modified PVC on thickness of the membranes is shown in Fig. 12. The modified membrane thickness tends to be increased at higher polymer concentration. The thickness is increased from about 0.07 mm to about 0.073 mm with the increase of the polymer concentration from 14 to 18 wt.%. Moreover, the thickness of 14 wt.% neat PVC membrane (0.07 mm) is higher than that of the membrane prepared from 14 wt.% modified membrane as shown in Fig. 12. Ortiz et al. [69] found that increases of the polymer concentration in the casting solution help to increase the membrane thickness.

3.6. VMD performance of neat PVC and PEA-g-PVC modified membranes

The effect of the polymer concentration of the PVC and PEA-g-PVC modified membranes on the membrane performance was examined by using a VMD system. The VMD process was tested using double

distilled water as a feed under different feed temperatures (i.e., 25, 40, 50 and 60 °C) and permeate vacuum pressures (i.e., 2, 10, 20, and 30 mbar) with feed flow rate of 40 L/h.

3.6.1. Effect of feed temperature

The effect of different feed temperatures (i.e., 25, 40, 50, and 60 °C) of PVC and PEA-g-PVC modified membranes on the permeate flux at the permeate side pressure of 2 mbar is illustrated in Fig. 13. The permeate flux, for 18 wt.% PEA-g-PVC membranes, increases from 1.9 to 4.42 kg/m² h with an increase of feed temperature from 25 to 60 °C. These values are higher than those observed for the membrane prepared with unmodified PVC that showed an increase from 1.2 to 2.52 kg/m² h when increasing the feed temperature from 25 to 60 °C. If we compare the properties of the two membranes, the improvement in flux of the modified PVC can be attributed to its higher hydrophobicity, which reduces the phenomena of partial wetting that, on the contrary, can occur with PVC, especially at the low vacuum pressure used during the experiment. Moreover, the pore size of the membrane was also very effective on the improvement in permeation flux. Nevertheless, the modified PVC membrane (14 wt.% PEA-g-PVC) at the same PVC concentration showed a more significant increase in the permeate flux, that ranged from 8, 10 to 37.5 kg/m² h at 25 and 60 °C, respectively. This result is due to a combination of factors such as; high contact angle and porosity, as shown in Figs. 9 and 10, respectively, as well as lower membrane thickness (see Fig. 12). Also this improvement in flux can be attributed to a combination of membrane properties: the 14 wt.% PEA-g-PVC is characterized by the highest porosity and lowest thickness. Moreover, it is also due to the largest pore size (around 0.37 μm) that if on the one hand can contribute to the flux. However, during the experimental tests, no wetting phenomena were registered. The permeate flux increases with increasing of feed temperature because the actual driving force for MD is the vapor pressure difference across the membrane and any increase in feed temperature will increase the vapor pressure of the feed solution, thereby trans-membrane vapor pressure is increased, resulting in a higher flux [70–72].

3.6.2. Effect of vacuum pressure

Effects on the permeation flux of the PVC and PEA-g-PVC modified membrane of different vacuum pressures in the permeate side (i.e., 2, 10, 20, and 30 mbar), under constant feed temperature of 40 °C and feed flow rate of 40 L/h, are shown in Fig. 14. Regarding the permeation flux of the membrane prepared with 14 wt.% PVC, a little increase in the permeation flux is observed, from 1.3 to 1.8 kg/m² h, at a vacuum pressure of 30 and 2 mbar, respectively. This range slightly increases for the

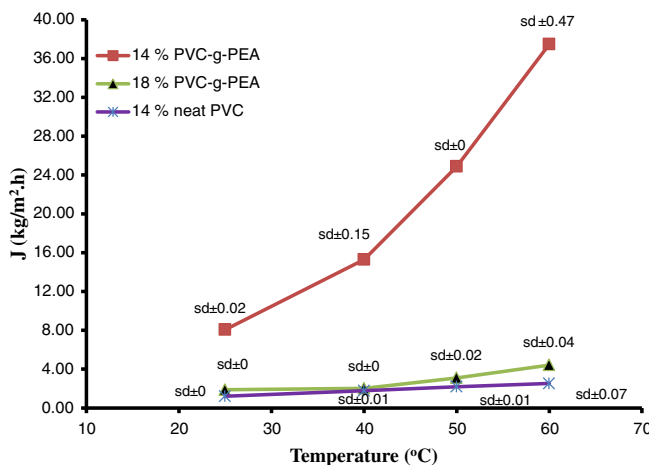


Fig. 13. VMD flux versus feed temperature for different concentrations of PVC-g-PEA membrane (14%, 18 wt.%) and 14% neat PVC. ([sd] is standard deviation).

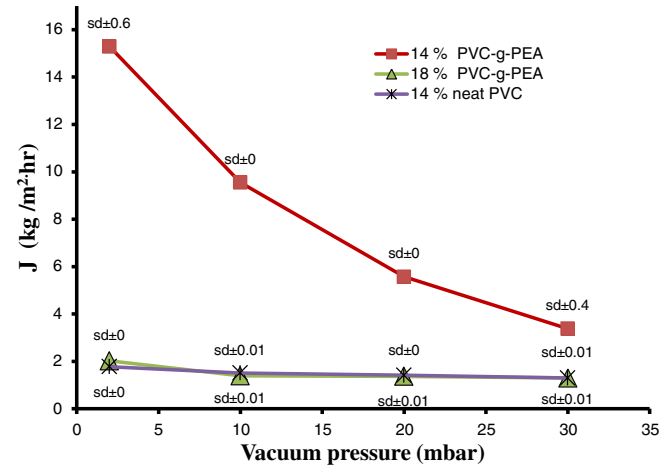


Fig. 14. Effect of vacuum pressure on VMD mass flux at feed temperature of 40 °C for neat and modified PVC (PVC-g-PEA) membranes. ([sd] is standard deviation).

Table 2

Separation performance of flat-sheet VMD membranes recently reported in the literature.

| Membrane flat sheet | Thickness (μm) | Temp. ($^{\circ}\text{C}$) | Flow rate (l/h) | Vacuum pressure (mbar) | Feed solution | J ($\text{kg}/\text{m}^2 \text{ h}$) | Ref. |
|-------------------------|-----------------------------|------------------------------|-----------------|------------------------|-----------------------|--|-----------|
| WG ^b | 68.3 | 25 | | 16.6 | D.W. ^a | 13.28 | [72] |
| GVHP ^c | 68.3 | 25 | | 16.6 | D.W. | 5.05 | [72] |
| PP | 163 | 60 | 18 | – | H ₂ O–(EG) | 10 | [73] |
| PP | 163 | 60 | 40 | – | H ₂ O–(EG) | 12.2 | [73] |
| PP | 163 | 60 | 48 | – | H ₂ O–(EG) | 13.5 | [73] |
| –PP commercial | 91 | 59.2 | 235 | 10 | D.W. | 56.2 | [74] |
| –PP longitudinal module | | 59 | 200 | | | 48.8 | |
| iPP ^d | 200 | 70 | 50 | 30 | D.W. | 28.92 | [75] |
| PTFE/PVA 1:1 | 43.6 | 70 | 32 | 20 | H ₂ O | 3.42 | [76] |
| PTFE/PVA 2:1 | 45.2 | 70 | 32 | 20 | H ₂ O | 9.45 | [76] |
| PTFE/PVA 4:1 | 47.4 | 70 | 32 | 20 | H ₂ O | 7.37 | [76] |
| PVDF | | 59.2 | | 16.6 | D.W. | 18 | [77] |
| PTFE | 175 | 60 | 120 | 70 | D.W. | 25.61 | [78] |
| PVDF-PTFE | 98 | 70 | 90 | 3 | D.W. | 35 | [79] |
| 14% PVC-g-PEA | 77 | 60 | 40 | 2 | D.W. | 37.5 | This work |

^a D.W. = distilled water.^b WG = PVDF/DMAc/5.95% H₂O.^c Membranes supplied by Millipore with the trade name Durapore, pore size = 0.22 μm for GVHP membrane.^d Isotactic polypropylene.

18 wt.% PEA-g-PVC modified membrane, whereas for the 14 wt.% PEA-g-PVC modified membrane the permeate flux increases more evidently from 3.38 $\text{kg}/\text{m}^2 \text{ hr}$ to 15.29 $\text{kg}/\text{m}^2 \text{ h}$ at 30 and 2 mbar, respectively. The registered trend confirms what was found during the tests at different temperatures and can be explained in terms of the superior membrane properties (porosity, pore size, thickness, contact angle) when moving from the 14 wt.% PVC membrane to the set of the grafted membranes. Within the grafted membranes, lower contents of PVC seem to provide membranes with better performance in VMD. Concerning the effect of the vacuum pressure, higher flux is obtained at low vacuum, because of the significant increase in the vapor pressure difference between the feed and permeate side. Actually, at constant feed temperature, the equilibrium vapor pressure of the water on the surface of the membrane at the feed hot side is constant and as the vacuum level increases (the pressure of the permeate side drops), the driving force across the membrane increases, which in turn leads to higher mass fluxes.

On the basis of the obtained results, the modified membranes prepared showed a significant improvement of the performance of VMD.

A comparison between the mass flux performances of the modified PVC membranes prepared in this work and the values reported in the literature for various polymeric membranes in flat-sheet configuration is presented in Table 2. It can be noticed that the PVC membranes prepared by the introduction of ethyl acrylate (EA) monomer onto the PVC by free radical graft copolymerization have a comparable and often better mass flux performance with respect to most membranes prepared from different polymer materials. This result is attributed to the combination of higher porosity, lower thickness and higher pore size, together with improved hydrophobicity, of the modified PVC membrane prepared by using the method aforementioned.

4. Conclusions and future research

In the present work, chemical modification of PVC by graft polymerization of EA was successfully carried out with free radical copolymerization catalyzed by benzoyl peroxide. Flat-sheet membranes from PVC and grafted PVC solutions were prepared via immersion precipitation process for VMD application. The effects of polymer concentration on the structural morphology, hydrophobicity, porosity, pore size, and mass flux of the modified membranes were evaluated. The following conclusions were found:

1. New absorption peaks were detected by FTIR analysis for the grafted copolymer at 1732 cm^{-1} , 1101 cm^{-1} , and 1022 cm^{-1} , which

indicated the introduction of the ester group of EA onto PVC backbone.

2. EDX analysis results revealed that both the increasing of the percentage of carbon and the appearance of oxygen demonstrates the existence of the ester group of EA onto PVC backbone.
3. Porous structure on the top surface of the membrane prepared from modified 14 wt.% PVC was observed due to the lower solution viscosity compared with other membranes prepared from different polymer concentrations of neat and modified PVC.
4. The layer near the top surface of the membrane was changed from large ellipsoidal voids with a sponge-like structure inside to finger-like structure and some sponge structure disseminated between them with increasing of polymer concentration for modified membranes.
5. The EA grafting onto PVC at different PVC concentrations results to an increase in the porosity, pore size and contact angle of the membranes, with a reduction of the membrane thickness. The VMD permeate flux of the PVC-g-PEA membrane was significantly improved with respect to the unmodified PVC membranes. The maximum permeate flux (37.5 $\text{kg}/\text{m}^2 \text{ h}$) was obtained at 60 $^{\circ}\text{C}$ with the 14 wt.% PVC-g-PEA membrane, thanks to the combination effects of porosity, large pore size and thickness of the membrane.

Based on the promising results obtained, future research will be addressed to evaluate the membrane performance in time by carrying out VMD tests on salty solutions and/or other aqueous feeds of interest.

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