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Effect of Polyvinyl Pyrrolidone on Polyvinyl Chloride-Graft-Acrylamide Membranes

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KEYWORDS

Polyvinyl chloride, acrylamide, grafted polymer, and polyvinyl pyrrolidone (PVP).

ABSTRACT

Polyvinyl-chloride (PVC) was dehydrochlorinated by alkaline-solution (NaOH) in determining molarity (3.0 M) followed by grafting with acrylamide (AM) monomer onto dehydrochlorinated PVC (DHPVC) backbone by free-radical graft copolymerization to produce new grafted polymer referred as graft 3M. Then investigated the effect of polyvinyl pyrrolidone (PVP) addition on the grafted polymer. Membranes from pure PVC, graft 3M, and graft 3M/ PVP were synthesis via a phase inversion method. The successful AM grafting onto PVC was confirmed by characterization of the membranes by Atomic Force Microscopy (AFM) and Field Emission Scanning Electron Microscope (FESEM) analysis, porosity, pore size, and contact angle measurements. The new synthesis (graft 3M) and (graft 3M/ PVP) membranes show excellent hydrophilicity in compared to pure PVC membranes, confirmed by higher pure water flux (PWF). The graft 3M/ 3wt.% PVP membrane exhibited the highest pure water permeate flux was about 540 L/m^2 h at 28 °C of feed temperature and 1bar of pressure, i.e. was improved by about 270 times compared to the unmodified PVC membrane and 2.35 times compared to the graft 3M membrane.

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1. Introduction

Many factors affect the selection of separation operation depending on the process's ability to solve a given problem. Nevertheless, a pair of general criteria is applied to the whole all separation operations; they should be feasible economically and should be feasible technically [1]. The interest in the membrane separation processes which began in the late 1960s was depending on: the capability to manufacture selective, high flux, necessary defect-free membranes on a big scale, and the capability to shape such membranes in the compact, high-surface-area, and economical membrane modules [2].

The species transport rate during a membrane is proportionate inversely to thickness of membrane. High rates of transport are preferred in the membrane separation operations for economic purposes; so, the membrane thickness should be possibly too thin. The evolution of the novel synthesis technologies of the membrane to manufacture anisotropic membrane structures was the main breakthrough of the technology of membrane through the last four decades. These membranes contain a highly thin surface layer, which is supported on a highly thicker, porous sub-structure. This layer and its sub-structure may be shaped in a single process or individually. The properties of separation and the rates of permeation of membrane are exclusively obtained via the layer of surface; the sub-structure acts as mechanical support. The higher fluxes benefits supplied via anisotropic membranes are too vigorous that approximately the whole commercial operations employ these membranes [3,4]. The membranes could be classified depending on the driving force of the specific separation process. When the pressure difference across the membrane was the driving force, membranes are significantly differentiated depending on the size of the molecules being separated and on the pore sizes of the membrane itself. Thus they can be divided into three major classes: Microporous include microfiltration (MF) and ultrafiltration (UF). Nanoporous include nanofiltration (NF) and reverse osmosis (RO). And Dense membranes include pervaporation (PV), Gas separation (GS). MF-membranes with higher pore sizes about (0.1- 5 μm) and likely to use for particles remove asbestos and many cellular materials like red blood cells and bacteria ranging from (0.1- 10) μm in diameter. ultrafiltration (UF) with small pores about (0.01- 0.1 μm) which able to separate large particles and micro-organisms and other particles with sizes ranging about (0.01- 0.2 μm). UF membranes had many uses in wastewater treatment, water reprocessing, food remediation, separation of protein, and beyond [3,5]. NF-membranes are porous and can filter types with size ranging about (0.001 - 0.01 μm). This means organic species and viruses removal. RO-membranes were highly dense and its pores mean as non-porous about (0.0001- 0.001 μm). So, RO-membranes could filter molecules with a low molecular weight such as aqueous inorganic solids, also organic-molecules [6-8]. A pervaporation process was used to separate liquid mixtures. A heated feed liquid mixture contacts one side of a membrane; permeate vapor is removed from the other side. Most gas separation processes using polymeric membranes with extremely thin selective layer to achieve economical fluxes. Early GS membranes were synthesis by cellulose-acetate (CA) membranes modified which produced for RO by the Loeb Sourirajan phase inversion process [9,10].

2. Experimental work

I. Materials

Table 1 summarizes all materials used in this work with its properties.

Table 1: The materials used in the experimental work.

Materials	properties
Polyvinyl chloride (PVC)	K Value: 65-67 Bulk density: 570 kg/m^3 Partical size: 250 μm Company: KSA by Sabic (Saudi Basic industries corporation)
Sodium hydroxide (NaOH)	Molecular Weight: 40,00 Assay(acidimetric):99,0% Company: Scharlau (Spain)
Acryl amide, Extra pure	Molecular Weight: 71.08 Company: HiMedia (India)
Benzoyl peroxide (BPO) with ~ 25% of H_2O	Molecular Weight: 242.23 g/mol Min. assay: 98.0% Company: HiMedia (India)
Cyclohexanone	Color: Colorless Company: BDH Chemicals Ltd (Poole, England)
methanol	Assay: 99.5% Company: Scharlau, (Spain).

N,N Dimethylacet amide (DMAC)	Purity: 99% 1 L ≈ 0.94 kg Company: Riedel-de Haen AG Seelze Hannover (Germany)
Polyvinylpyrrolid-one K 15 (PVP)	Molecular Weight:10,000 Loss: ~5% loss on drying, 20 °C (HV) Company: Fluka , Sigma-Aldrich Chemie GmbH (United States)
Glycerol	Assay > 99.5% Water < 0.5% Company: Romil LTD. Pure Chemistry.
Deionized water	TDS: (0-2) From Commercial market

II. Dehydrochlorination and grafting of PVC and purification of the result

Dehydrochlorination, grafting of PVC and purification of the result was carried on in the laboratory by using a reflex system by the following procedure as in our previous work [11,12]:

1-Preparation NaOH solution in 3 molarity.

2-PVC was dried then weighting 10g of it and immerging in (100 ml) 3 molarity NaOH solution within around bottom flask with continuous stirring for 8 hours after reaching its boiling temperature.

3-Until the temperature of the liquid reaches to R.T, filtering the result and washing it several times to remove all traces of alkali solution and shoring that by PH paper.

4-Drying the result in R.T. until a DHPVC 3*M* powder obtained, and complete drying in a vacuum oven at 55°C for 24 hours.

5-Weighed quantity of the dried DHPVC 3M (3 g) was dissolving in 25 ml cyclohexanone under N2 atmosphere with a reflux condenser on stirring at R.T. for 8 hours to obtain a good dissolving.

6-An BPO solution was prepared by dissolving 0.45 g of it in 10 ml cyclohexanone. Also, AM solution was prepared with dissolving 3 g of it in 25 ml cyclohexanone. The BPO solution was added directly to dissolve DHPVC and raise the temperature to 70 °C while AM solution put in dropping funnel and gradually added.

7-After 3 hours, the reaction was complete and the mixture left to cooled and then poured into methanol to precipitated the result. Followed by filtration and washing by methanol, and drying by vacuum oven.

8-The result mixture was purification in D.I. water by stirring at about 50 °C for 1 hour to release the polyacrylamide (PAM) homo-polymer and obtained the solid grafted copolymer (PVC-g-PAM). Followed by filtration and washing four times to ensure complete homo-polymer removal and drying by vacuum oven at 60 °C for 30 hours.

III. Membrane Preparation

The asymmetric flat-sheet membranes were synthesis by the immersion precipitation phase inversion method. According to the literature [13-16], the casting solutions were prepared in DMAC solvent by dissolve 15 wt.% of pure PVC and graft 3*M*. While preparing graft 3*M* / PVP membranes**,** graft 3*M* solution was prepared in three different ratios (14, 13, 12% wt.) and PVP additive was added in three different ratios (1, 2, and 3 % wt.) to the dissolved solution, respectively. After 24 h stirring at R.T. to prepare, homogenizes and completely dissolved polymer left it 12 h degassing. Then, cast the polymer solutions with 300 μm casting knife onto a clean glass-plate at R.T. After 60 Sec., the films were immersed into a coagulation bath (deionized water) at 28°C, each membrane takes a special separation time from the glass plate. The separated membrane left for 24 h and then transferred into a second fresh deionized water and kept for 48 h to remove the left solvent and complete phase inversion method. Finally, the membrane immersed in 15% glycerol solution tank for 24 h, then lifted it to drying in R.T. for 24 h.

IV. Characterization

Atomic Force Microscopy (AFM)

The surface morphology (2D and 3D topographic images), and the flat sheet surfaces were characterized in terms of pore size (i.e. mean pore size and pore size distribution) and roughness analysis of mean roughness (Ra). The AFM device, Angstrom, Scanning Probe Microscope (Spm), Advanced Inc, (AA 3000A°, USA). Small pieces of the prepared membranes (1×1 cm) were cut and glued on glass substrate. The membrane surfaces were scanned with image size (10109 nm, 10170 nm) and topography pixels (500,503).

Field Emission Scanning Electron Microscope (FESEM)

The top surface and cross-sectional morphology of the all prepared membranes were examined by using FESEM (FEI manufacturer, Nova Nano 450 model, 1.4 nm resolution, 35X to 1,000,000X magnification, electron Gun was FEG with ultra-high brightness Schottky field emitter, extracting voltage (Vext) was from 0 to 5kV, and acceleration voltage (Vacc) was at 50 eV to 30 kV). Small pieces were prepared by cutting from the produced membrane using liquid nitrogen.

Porosity and Pore Size

Membrane porosity was determined using Eq. (1) [13,15-18]:

$$\varepsilon(\%) = [(mw - md) / (\rho Ad)] * 100 \qquad (1)$$

The calculation of porosity is based on measuring the wet mass (mw) and dry mass (md) of the membrane sample. ρ , A and d are the water density, membrane area, and membrane thickness respectively. Guerout-Elford-Ferry equation was used to determine the mean pore radius of the membrane (r_m) [13,15,19]:

$$rm=\sqrt{[(2.9-1.75\varepsilon)\, 8\eta dQ)/ (\varepsilon\, A\, \Delta P)]} \qquad (2)$$

where η , Q and ΔP are the water viscosity, pure water flux, and operation pressure respectively.

Water Contact Angle

Contact angle measurement was used to investigate the hydrophilicity of the membranes. The contact angle was measured by an Optical Dynamic I Static Interfacial Tensiometer & Contact Angle Meter (SL 200C, KINO Industry Co., Ltd., USA) at three different locations and the average value was taken.

Pure Water Flux

The pure water flux (J) of a membrane with an effective area (A) was determined by measuring the volume of pure water (V) passing through the membrane within Δt interval ambient temperature. Equation (3) was used to calculate the pure water flux [13,18]:

$$J = V / A\, \Delta t \qquad (3)$$

3.Result and Discussion

I. AFM

Figure 1 displays 2D and 3D AFM images of the top surfaces of the prepared membranes (pure PVC, graft 3*M*, graft 3*M*/ 1wt.%PVP, graft 3*M*/ 2 wt.%PVP and graft 3*M*/ 3 wt.%PVP). Where the shining areas clarify the highest sites of the membrane surface, while the blackish areas denote holes (valleys) or pores of the membrane. As mention in Table 2, the surface roughness parameters of graft 3*M* membranes were highly increased with R_a values about (20 nm) is compared to pure PVC membranes (11.1 nm). The PVP additive led to some lowering in the surface roughness parameters of graft 3*M* membranes at 1wt.% and 2wt.%, but the good effect was showed at 3 wt.% with R_a value about (36.1 nm). This increase may be due to the larger pores formed on the membrane's top surface and led to the formation of humps and valleys with a positive influence on surface roughness, where the rougher surface would be the favorite one in permeation and hydrophilicity. Thus, the increase in surface roughness of the membranes led to pore size and porosity increasing, which means an increase of flux. This results following literature [20, 21].

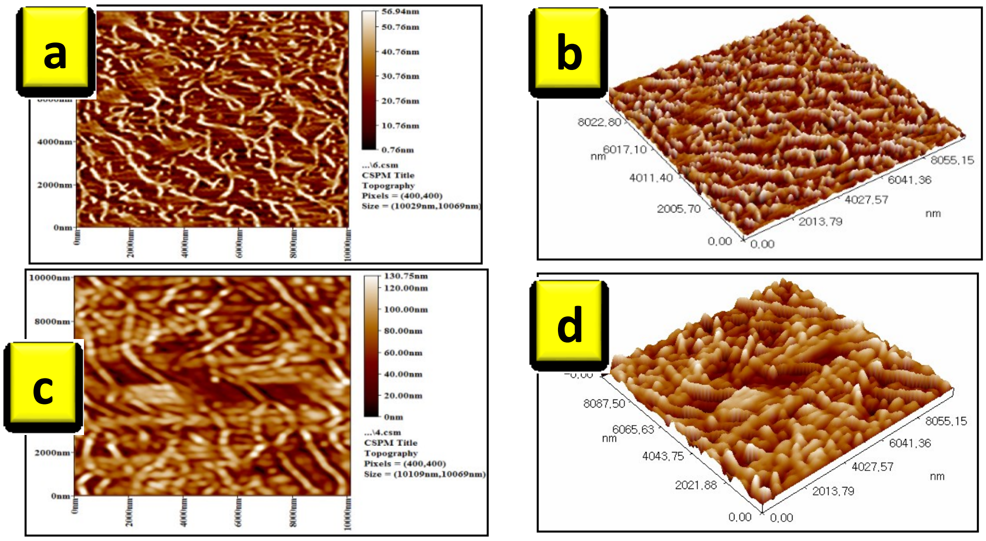
Table 2: Roughness parameter of prepared membranes.

Sample	Roughness parameter		
	Ra(nm)	**Rq(nm)**	**Rz(nm)**
Pure PVC	11.1	13.4	56.2
Graft 3M	20	24.7	70.8
Graft3M/ 1%PVP	14.8	17.4	63.2
Graft3M/ 2%PVP	10.3	12.6	60.9
Graft3M/ 3%PVP	36.1	44.5	222

II . Field Emission Scanning Electron Microscope (FESEM)

From all FESEM images, noted that the characteristic structure of membranes prepared via phase separation method which gave the asymmetric structure of all prepared membranes, from the dense top layer to the porous bottom supported layer with different pores shapes and pore size. Is noted that the morphologies of the prepared membranes were altered after grafting with hydrophilic monomer and after the addition of different percent of PVP, which led to a significant effect on the permeate flow and other membrane properties. The top surface and cross-sections morphologies of pure PVC, graft 3*M*, graft 3*M*/ 1%PVP, graft 3*M*/ 2%PVP, and graft 3*M*/ 3%PVP membranes were investigated, as shown in Figure 2, at 5µm magnification for top surfaces (left images) and 50µm magnification for cross-sections (right images). The pore structure of the prepared membranes is expected to be a function of many variables, such as casting solution viscosity, the process of liquid-liquid demixing depending on both affinity and miscibility, the presence of additives and nanoparticles [22-26].

The grafting improved the formation of macro-voids and pores in surfaces and cross-sections as showed at graft 3*M* membrane in Figure 2 (c, d), respectively. Larger top surface micro-voids and from cross-section image noted that the large interconnected finger-like pores structure extended from the top layer to the bottom supporting layer. Compared to the graft 3*M* membrane, all of the blended membranes showed the more interconnected finger-like structure of pores in the cross-section images. Where the higher improvement was observed at 3 wt. %PVP for both top surface macro- voids and cross-section morphology with continuous finger-like pores as in Figure 2 (i,j), respectively. Similarly with literature about PEG additive [27], but the lower effect of PVP was noted at 1wt.% PVP, just; on the micro-voids of the top surface.



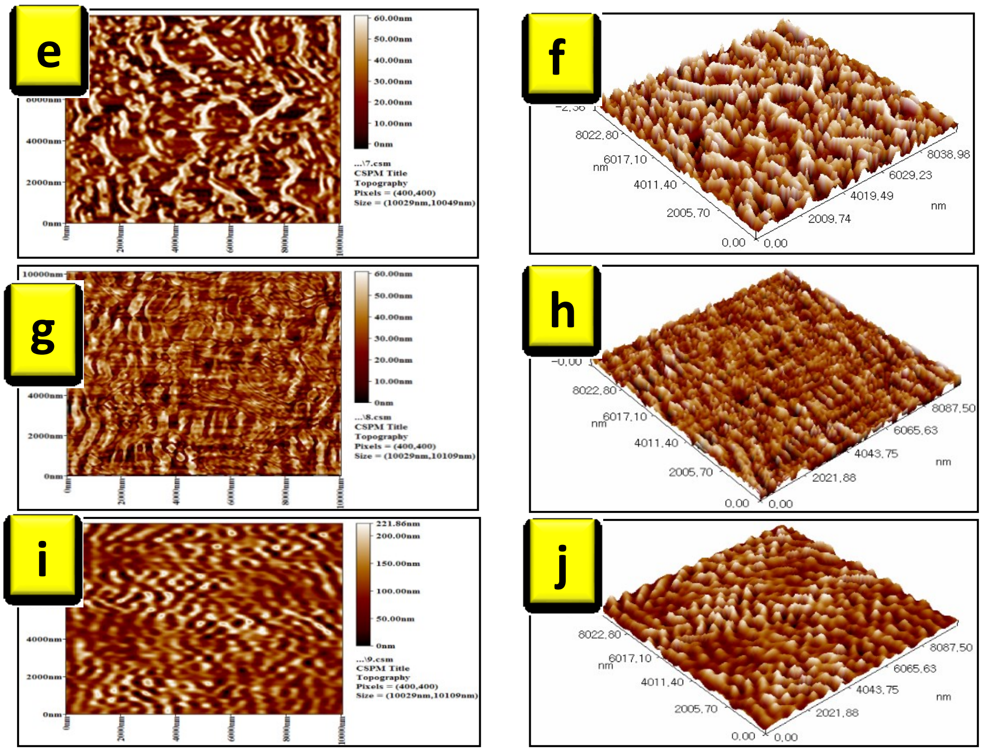
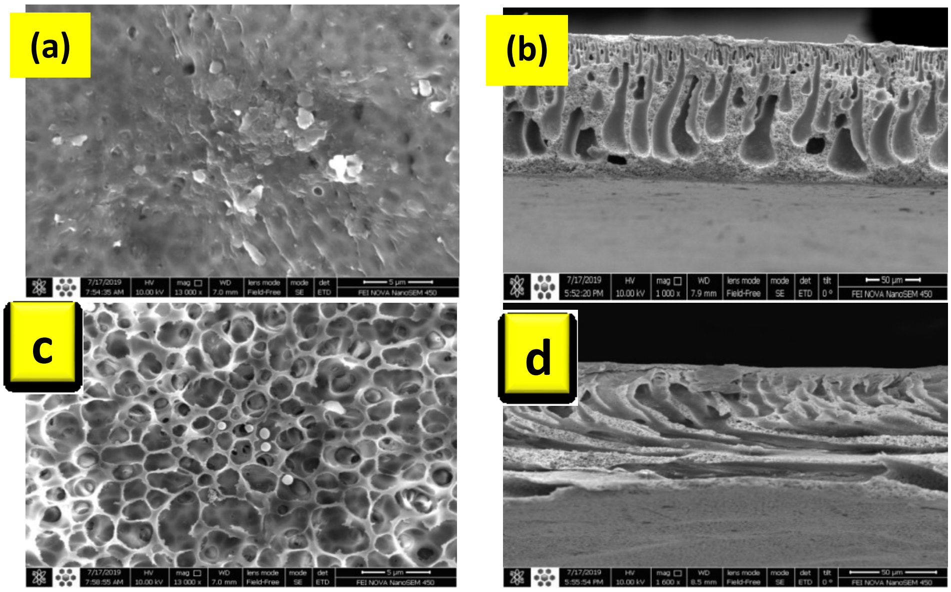


Figure 1: 2D and 3D AFM images of pure PVC (a)(b), graft 3M (c)(d), graft 3M/ 1% PVP (e)(f); graft 3M/ 2% PVP (g)(h); graft 3M/ 3% PVP (i)(j) membranes; respectively.

III. Porosity and mean pore size of prepared membranes

Chemical modification of membranes with acrylamide grafting led to membrane thickness increasing with constant polymer concentration in casting solution so that porosity increased. As provided from AFM and FESEM results about to create more surface macro-voids and cross-section fingers like pores in grafted membranes and modified grafted membranes with PVP additives, result in high porosity and pore size. Delayed de-mixing of graft 3*M* and graft 3*M*/ PVP membranes led to porosity changes related to pore size changes as reported previously [28, 29].



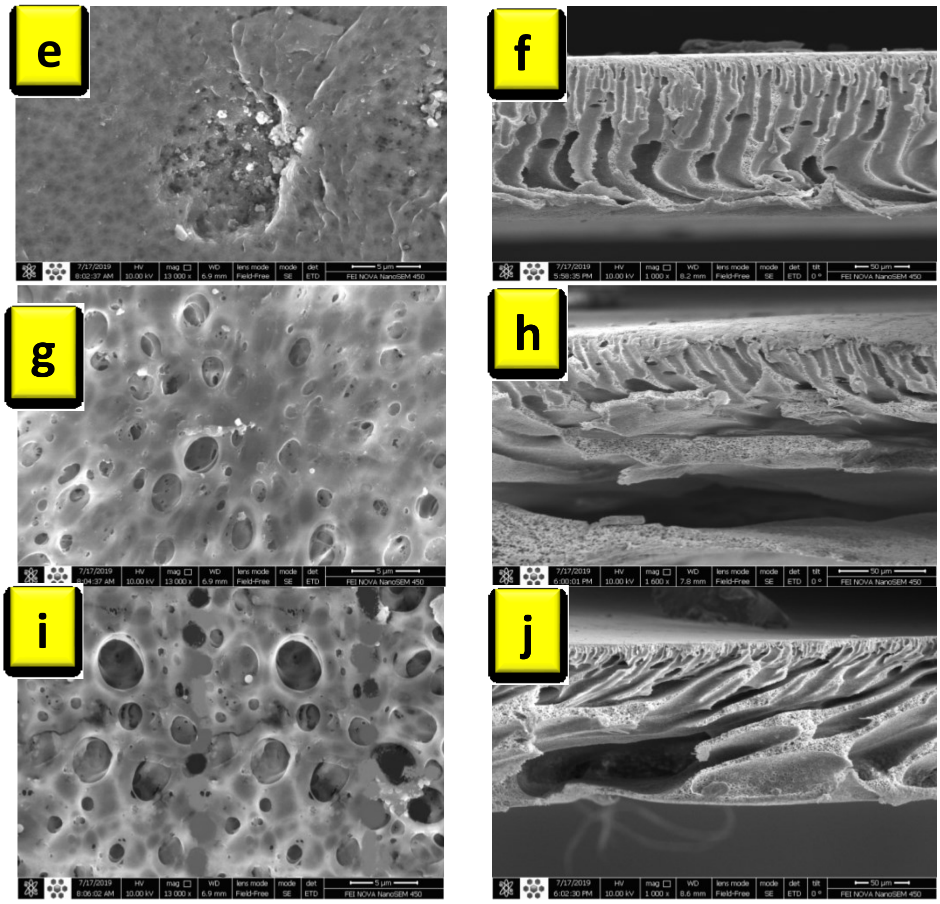


Figure 2: FESEM images of membranes. Left: top surfaces (5µm), right: cross sections (50µm) of pure PVC (a)(b), graft 3M (c)(d), graft 3M/ 1% PVP (e)(f); graft 3M/ 2% PVP (g)(h); graft 3M/ 3% PVP (i)(j) membranes; respectively.

The porosity and mean pore size calculation for prepared membranes by Eqs. (1) and (2), respectively, as displayed in Figure 3 for pure PVC, graft 3*M*, and graft 3*M*/ PVP membranes. A clear increase in the porosity of the grafted membrane, from (9.2 %) for pure PVC reached the value (67.2 %) at graft 3*M* membranes. Also, the mean pore size of the graft 3*M* membrane shows increment ranging from (11.1 nm) for pure PVC to (47.3 nm). And the continuous increase in porosity and mean pore size of graft 3*M*/ PVP membranes with increasing PVP weight percent, reached higher value at 3wt.% PVP about (75 %) porosity and (57 nm) mean pore size. Due to the pore agent addition (PVP) which left the membrane after immersion in water coagulation bath by dissolving in water and create behind it more porosity and larger pore sizes.

By coinciding the mean pore sizes values of all prepared membranes with ultrafiltration (UF) which have smaller pores sizes about (0.01 - 0.1 µm), confirm that the all resulted membranes were ultrafiltration membranes. UF has different applications in wastewater treatment, separation of protein, and others [3].

IV. Contact angle and pure water flux of prepared membranes

The hydrophilicity of membranes was investigated by measuring the static water contact angle according to the Young-Laplace fitting mode, a lower contact angle (CA) means that the surface of the membrane is more hydrophilic. With less than 90° contact angle, water can penetrate the pore without more pressure. But pressure increasing was important with CA is larger than 90° [3,30].

The measurement of CA done after 1 sec. and 30 sec. from droplet falling as shown in Figure 4, the graft 3M membrane shows hydrophilicity enhancement by CA lower than pure PVC membrane, is around (80° and 79.2° after 1 sec. and 30 sec., respectively), proved that grafting success with the hydrophilic monomer to reach value about (60° and 58.3° after 1 sec. and 30 sec. from droplet dropping, respectively) for graft 3M membrane. All blended (Graft 3*M*/ PVP) membranes showed a continuous decrease in contact angle with PVP weight percent increasing to reached the great decreasing at 3% PVP with contact angle about (47.5° and 46° after 1 sec. and 30 sec. from droplet dropping, respectively). This lowering in contact angle because of blending with more hydrophilic PVP, water-soluble polymer that washed out of the matrix during membrane formation and subsequent operation. Therefore, PVP commonly used to increase the hydrophilicity, porosity, and permeate flow of asymmetric membrane during membrane fabrication [31-35].

The fluxes data of prepared membranes, as shown in Figure 5, were measured with 1 bar fixed pressure by (cross-flow) mode system at R.T. The data shows a very good flux enhancement in contrast to pure PVC membrane, which synthesis from commercial PVC powder, and exceeded the other enhancements or on similar with other UF-PVC membranes as in membranes modifications literatures [16,18, and 36].

These excellent flux enhancements are a result of grafting with the hydrophilic monomer (AM) having high polarity in the successful reaction by initiator graft-copolymerization. Where the graft 3*M* flux reached value about (230 L/m^2*h). The addition of PVP additives to graft 3*M* gave very well flux improvement at three different weight percent reaches about (265, 325, and 540 L/m^2*h) at (1, 2, and 3 wt.% PVP) respectively. This improvement due to pore agent addition (PVP) led to create interconnected pores in cross-section structure and surface micro-voids as shown previously.

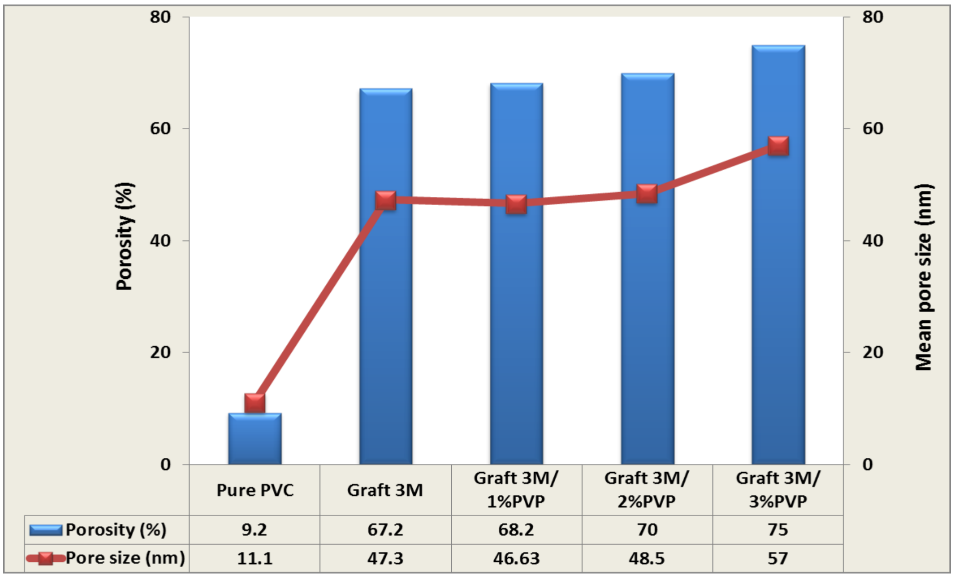


Figure 3: The porosity and mean pore size of prepared membranes.

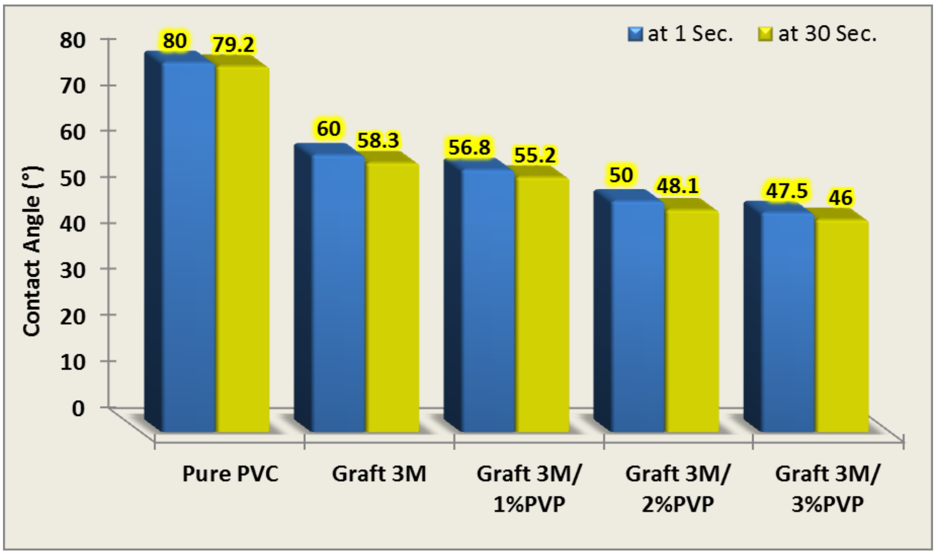


Figure 4: The contact angle (CA) of prepared membranes at 1st Sec. and 30 Sec.

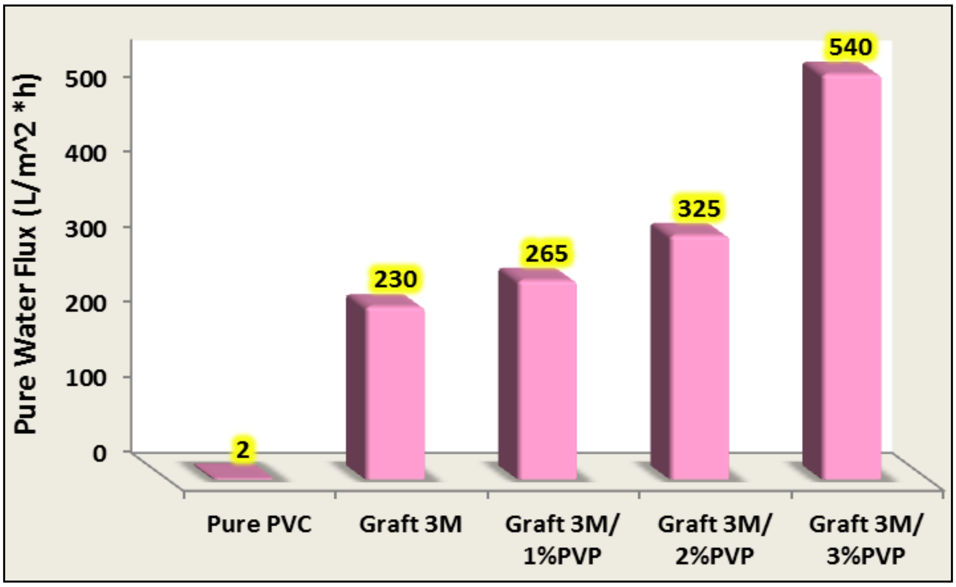


Figure 5: Pure water flux of prepared membranes.

4. Conclusions

The results of the AFM and FESEM analysis display that the successful grafting polymerization with AM on DHPVC 3*M*. The Graft 3*M* and Graft 3*M*/ PVP membranes display higher porosity and pore size increasing with the maximum value at 3wt.% PVP. Also, the Graft 3*M* and Graft 3*M*/ PVP membranes display excellent hydrophilicity enhancement with contact angle (CA) lower than pure PVC and higher pure water flux. The graft 3*M*/ 3wt.% PVP membrane showed the highest pure water permeate flux was about 540 L/m^2*h (enhanced by about 270 times) in contrast to the unmodified PVC membrane and the result confirms that all new synthesis membranes were ultrafiltration-membranes UF.

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