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Compatibility of PVC/TEA Blends Membranes
Preparation, Characterization, Evaluation and Their Water Permeation
Properties

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Abstract

Triethanol amine (TEA) was introduced as a modifier to hydrophilize poly vinyl chloride (PVC) and enhance the permeation flux by changing the membrane morphology. (PVC/ TEA) have been prepared by solution blending. The compatibility and the miscibility of PVC/TEA blends in THF were studied and characterized. Modifications of the surface morphology, wet ability and porosity are proved by scanning electron microscope (SEM) images, contact angle measurements and permeability, respectively. It was found a better wet ability, permeability, and porosity of the modified PVC films than that of the membranes made from pure PVC. PVC/TEA membranes were characterized by FTIR, morphologically using SEM, thermally using TGA, and mechanically using universal testing machine. Permeation flux of PVC/TEA membranes was 10947 L/D/M2 and salt rejection performance for mono layer membrane was 33.7 % for 3%NaCl solution. Ion exchange capacity (IEC) for (PVC/TEA) membrane was 2.5 meq/gm., whereas contact angle and water uptake were 44.12 and 21% at room temperature, respectively. The results showed that the permeate quality and quantity are almost stable upon long run, thus PVC/TEA membranes can be used effectively for water treatment purification.

Keywords: Triethanol amine; modifier; Ion Exchange Capacity; Permeation flux; contact angle and water uptake.

1. Introduction

There is an increasing interest to the hydrophobic porous polymeric materials in the membrane technologies because of their stability during the work. The surface/fluid interface interaction is of great importance in this case. There is an increasing belief in the ability of the surface modification to change this interaction in a desirable direction. A lot of chemical methods for temporary or continuous hydrophilization of polymer surfaces have been developed up to now aiming at combining the stability of the hydrophobic porous materials with the advantages of the hydrophilic ones [1–4]. The polymeric membrane becomes more hydrophilic in the presence of inorganic fillers. The uniform dispersion of inorganic fillers in polymer matrix results in efficient mixed matrix membrane and exhibits benefits of both the inorganic and organic phase [5]. Ultrafiltration (UF) membranes are porous membranes with pore size ranging from 5 to 50 nm. The term ultrafiltration has

been introduced to discriminate the process whose nature lies between nanofiltration and microfiltration. Three modules of ultrafiltration can be obtained flat sheet, tubular and hollow fiber [6]. UF membranes are usually characterized by their molecular weight cut off (MWCO), which is typically defined as the molecular weight of a solute that has a rejection of 90%. The MWCO of UF membranes is in the range 0.3–500 kDa. The UF membranes are asymmetric membranes and the phase inversion method is a well-known technique for the fabrication of asymmetric membranes, which can be performed by almost all kinds of techniques such as nonsolvent-induced phase separation (NIPS), thermally induced phase separation, vapor induced phase separation, and evaporation-induced phase separation [7]. For removal of pollutants from groundwater, nanofiltration (NF) seems to be a suitable method as a process capable of removing hardness, sulphates, chlorides, and bacteria in one step. For preparation of

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polymeric nanofiltration membranes, the exchanging of solvent and non-solvent in coagulation bath plays an important role. Many researchers have investigated the effect of addition of various components on membrane performance and membrane structure. One of the most important parameters in membrane morphology and performance is polymer concentration. Preparation of nanofiltration membrane with low concentration of polymer (especially PVC) and effect of different concentrations [8]. It could be difficult to select the right membrane and membrane material for a given process, and some general information about the process environment must be available to make a proper selection. The first step is to determine the preferred process, reverse osmosis (RO), NF, UF or micro filtration (MF) then look at the available membrane materials. Literally all RO, NF and UF membranes are asymmetric. This differentiates most membranes from common filters, e.g. coffee filters, which are symmetric or, in other words, are identical on both sides of the filter. Membranes have a tight top layer facing the product to be treated. This layer is also called the skin layer. It is thin, typically <<0.1 micron. The membrane itself is 150 - 250 micron, the bulk of the membrane simply providing structural support for the skin layer. The asymmetric structure means that the pores are wider and far away from the surface, which prevents the pores from being plugged. This provides a good fouling resistance, since foulants tend to be either totally rejected or to pass all the way through a membrane. PVC is an outstanding polymer for the fabrication of UF membranes because of its interesting good characteristics, including stiffness, lower price, excellent physical properties and mechanical performance, and good thermal stability. In addition, it has strong chemical resistance to the solvents, inorganic acids, halogens, oxidants, and alkalis, which are widely used in industries. Another main advantage of PVC as a membrane material is its easy of dissolution in some organic solvents, such as N, N-dimethylacetamide, dimethylformamide, tetrahydrofuran, and N-methyl-pyrrolidinone (NMP). Since PVC is not soluble in water, PVC membranes can be easily fabricated by the phase inversion method [7]. Polymer blending, which include membrane preparation from mixture systems with two polymers with different properties, is a convenient, inexpensive, and versatile approach to improve both the membrane surface and internal pore walls by giving them desirable properties. Therefore, for preparation of UF membranes, PVC was blended with some polymers or copolymers. Also, incorporation of inorganic particles seems to be an effective manner to improve fouling resistance and performance of PVC UF membranes.

PVC membrane characteristics can be changed by a controlled grafting reaction. Even a small number of hydrophilic groups such as —OH or —COOH should be enough if they were situated on the walls of the pores [9]. Ultrafiltration (UF) membranes [7] were prepared from poly (vinyl chloride) (PVC) as main polymer, poly (vinyl pyrrolidone) (PVP) as additive, and 1-methyl-2-pyrrolidone (NMP) as solvent using Design Expert software for designing the experiments. The membranes were characterized by SEM, contact angle measurement, and atomic force microscopy. The performance of UF membranes was evaluated by pure water flux (PWF) and blue indigo dye particle rejection. The results showed that the increment in PVC concentration caused reduction of PWF. Moreover, at constant PVC concentration and if the concentrations of PVC were lower than 10 wt. %, the PWF reduced by increasing the concentration of PVP. However, at PVC concentration higher than 11 wt. %, increment in PVP concentration showed increment and reduction of PWF. In [8], (PVC) nanofiltration membrane was prepared by using Dimethyl acetamide (DMAC)/Tetrahydrofuran (THF) as solvents via the phase inversion method. The effect of solvents' mixing ratio (DMAC to THF) in the casting solution and phase separation time in coagulation bath on membrane flux and selectivity were studied. The membrane tensile strength measurement and scanning electron microscope (SEM) analysis were also carried out in membrane characterization. The highest membrane selectivity and flux were found at (85:15) solvents' mixing ratio (DMAC to THF). PVC was successfully casted as membrane and modified by Ar plasma [10] followed by grafting with ultra-thin film of polyacrylic acid. Such modified membrane maybe acts as an electrolyte membrane specially after grafting process with acrylic acid vapor followed by sulfonation process indicating by the increase of the water uptake values of membranes. A new kind of membrane was prepared by blending styrene-butadiene rubber (SBR) and natural rubber (NR) in equal proportions [11]. These membranes were crosslinked by four different vulcanising systems viz. conventional (CV), efficient (EV), dicumylperoxide (DCP) and a mixture consisting of sulphur and peroxide (mixed). The properties of these membranes were evaluated by pervaporation separation of chlorinated hydrocarbon and acetone mixtures. The experimental results showed that the selectivity and the fluxes of these membranes depended on the nature and distribution of crosslinks between the macro molecular chains of the membrane. The effects of feed composition and the molecular size of the permeate on the permeation flux and selectivity were investigated. The aim of the present article is to obtain a

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hydrophilic and fouling PVC resistance membrane. The bulk-modified PVC were synthesized from blending of PVC and TEA, then hydrophilic porous PVC membrane was prepared with well-defined pore sizes and fouling resistance through solvent evaporation technique method. The influence of operation time applied pressure on salt rejection and water flux were studied. Figure 1 gives a schematic representation for the aim of work of our current study.

Fig.1 Schematic diagram for the current study.

TEA
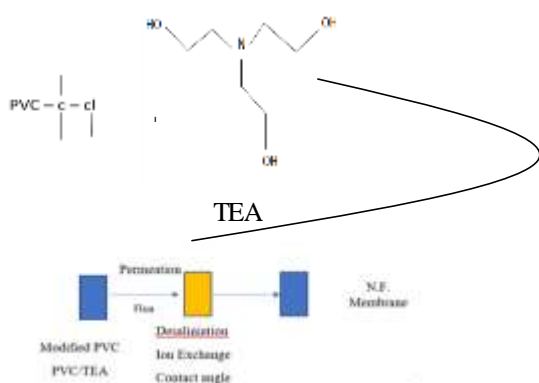
2. Materials and Methods

2.1 Materials

Polyvinyl chloride (M.wt. ~48000, fine powder) was imported from Belami fine chemicals. (India). Sodium chloride (Purity 99.5%, M.wt.58.44) was obtained from Sigma-Aldrich Chemicals Ltd. Germany. Tetrahydrofuran (THF) (Purity 99.9%, distilled) was purchased from Sisco research laboratories, India. Triethanolamine (TEA) Art. 822341, MERCK-Sehuchard, 8011 Hohenbrunnbei Munchen.

2.2 Preparation of PVC/TEA Membranes

PVC and the blended membranes of PVC/TEA were prepared by the solvent evaporation method. PVC/TEA (3 %, w/v) was dissolved in THF as a solvent casting solution mixture at 25 °C. After addition of TEA to the mixture with continuous stirring for 3hrs, the solution was casted on a horizontal glass plate at 25°C and, after a pre-determined evaporation time ranging from48-72h. The PVC/TEA membrane was removed gently from the glass plate and soaked into distilled water for 2hin order to remove any traces of solvent and also leave the glass plate smoothly. By changing the concentration of the polymer in the casting solution and the ratio between PVC and TEA, dissimilarity morphology properties, permeation, and transport properties could be observed. The average thickness of obtained membranes was 0.08–0.1 mm.

2.3 Instrumental Measurements

2.3.1 Wettability Measurements

Specimens of PVC/TEA membranes (1 cm ×1 cm) at random position were used for wettability measurements. Contact angles of PVC/TEA surfaces were measured with water drop on the surface of membranes by the contact angle meter. The average value of five measurements was taken at different locations on the surface. The hydrophilicity of the membrane is often measured through contact angle. It is one of the simplest available method for determining the hydrophobic or hydrophilic nature of chemical groups attached to the outer layer of a surface [12]. The swelling ratio or water uptake (WU) was determined by soaking the membrane samples in de-ionized water for 24 h at room temperature until swelling equilibrium was carried out. Samples were removed and the excess liquid adhered to both sides of their surfaces and quickly blotted by filter paper. The water uptake was determined as the weight of the membrane in the wet state compared to the dry state using eq. (1) [13]

$$Swelling\ ratio\ (\%) = WU(\%) = \left(\frac{W_w - W_d}{W_w}\right) \times 100 \quad (1)$$

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where W_d and W_w are the weights of the dry and the wet membrane samples respectively

2.3.2 Determination of Flux and Separation Rate

PVC/TEA membranes were tested in the membrane cell after pressurized under a pure water pressure of 200 KPa for 1 h. The pure water flux, permeation flux, and the rejection were then measured under the pressure of 200Kpa to 600Kpa at 20 °C. The pure water flux (PWF) and permeation flux (F), were calculated using eq. 2 [14]

$$F(PWF) = \frac{W}{At} \tag{2}$$

where the total weight of the water or solution permeated during the experiment; A is the membrane area, and t is the operation time. Rejection R was calculated using eq. 3 [15]

$$R(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \tag{3}$$

where Cp and C_f are the concentrations of permeate and feed, respectively. After filtration process, the whole test apparatus and the membrane sheet were rinsed thoroughly with de-mineralized water to remove any deposition.

2.3.3 Investigation of Surface Roughness

The surface roughness investigation of the PVC and PVC/TEA membranes used for water treatment applications is very important characterization tool. The average roughness was measured using surface roughness tester SJ- 201P, Japan. Samples were mounted onto a glass slide with double-sided tap. Minimum sample dimensions were 25mm × 25mm

2.3.4 Determination of Ionic Exchange Capacity (IEC)

The IEC determination was performed using the titration method. For the IEC measurements, the membranes in acid form (H+) was converted into Na+ form by immersing in 1 M of NaCl solution to liberate the H+ ions. H+ ions in solution were then titrated with 0.01 M NaOH and phenolphthalein indicator. The IEC is calculated from equations were discussed else, where [15]

$$IEC = \frac{V_{NaOH} \times N_{NaOH}}{W} \tag{4}$$

where V is the volume of consumed $NaOH$ solution and N is the normality of $NaOH$ and W is dried membrane weight.

2.4 Membrane Characterizations

2.4.1 FT-IR Spectra

Vacuumed and dried samples of PVC, and (PVC/TEA) membranes were analyzed by FTIR on an EQUINOX 55 instrument (BRUKER, Germany). Translucent KBr-disks were prepared by grinding the dried sample materials together with infrared grade KBr and then pressed. The FTIR spectra were obtained by recording clear deformation vibration after blending for Polyethyleneimine (PEI) and polyethylene glycol (PEG) with PVC. All samples were freeze-dried using liquid nitrogen, crushed to a fine powder (KBr: sample = 130 mg: 2 mg), and pressed by applying a force of 105 N into a transparent disk (maximum disk weight = 145 mg) with a diameter of 13 mm. All samples were measured in absorbance mode.

2.4.2 Thermal Stability by TGA

The thermal characterization of vacuumed-dried of PVC, and PVC/TEA membranes have been accomplished using TGA thermo-grams. The thermo-gravimetric analysis (TGA) was performed on a 204 Phoenix TGA instrument (NETZSCH, Germany) from 50 to 600°C at a heating rate of 10 °C/min. The onset temperature (T_{onset}) was determined by TGA thermo-grams. T_{onset} is defined as the temperature at the intersection of the baseline mass and tangent drawn to the mass curve at the inflection point or point of greatest rate of mass loss % [16].

2.4.3 Mechanical Properties

The maximum tensile strength and the elongation degree to break of PVC, and PVC/TEA membranes have been conducted using a tensile testing machine (model: AG-I/50–10KN, Japan). PVC and PVC/TEA membranes were cut into specific shape (40 mm long, 15 mm wide). The analysis was performed at a stretching rate of 10 mm/min with pre-load of 0.5 N to determine the load for each sample [17]. The thickness of membrane samples was measured with a dogmatic caliper before examination.

2.4.4. Scanning Electron Microscope (SEM)

The surface and internal structure of the prepared membranes samples were investigated by Analytical-SEM (type: JEOL, JSM-6360LA, Japan) with 15 kV voltage for secondary electron imaging. The samples were all dried in vacuum at room temperature, then frozen in liquid nitrogen and fractured. After plated with gold, they were transferred into the microscope. Membranes were dehydrated by freeze-dryer and coated with Au using an ion sputter coater (model: 11430, USA, combined with vacuum base unit or SPi module control, model: 11425, USA).

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3. Results and Discussion

In order to prepare polymer blend membranes with suitable pore size, the effect of different additive types such as inorganic, organic, and macromolecular nature as pore former on pure water flux PVC and the blended membranes of PVC/TEA were studied. Thus, different pore formers such as glycerol, ethylene glycol (EG), TEA or polyethylene glycol (PEG) as additives; could be used individually at different concentrations in the casted solution. TEA has been used as pore former in this work.

3.1 Effect of Ethylenediamine Concentration

3.1.1 Ion Exchange Capacity

The effect of TEA content in PVC/TEA membranes on ion exchange capacity was measured and illustrated in Figure 2.
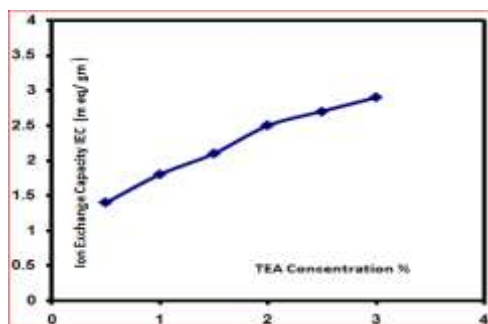
Fig. 2 The effect of TEA content in PVC/TEA Membranes on ion exchange capacity.

Different amount of TEA from 0.5 % to 3% was employed. It was shown that there is a clear increase from 0 to 2% of TEA which was attributed to increase the amine content of the prepared membrane. Beyond this concentration, a slightly increase in ion exchange capacity was observed. In fact, the compatibility of PVC and TEA solution starts to decrease which resulted in an increase the hydrophilicity of solution. In which case, a fast solution out of one of both polymers (TEA) from the reaction medium can recognized by precipitation of TEA outside the reaction medium and removed during washing step.

3.2 Water Uptake

The influence of different portions of TEA on membranes wettability was studied as shown in Figure 3. It illustrates swelling behavior of PVC/TEA that has been improved clearly with increasing the added amounts of TEA to 2 %. This behavior could be attributed to an increase in the hydrophilicity of membranes by increasing the amount of TEA which is in good agreement with the work of V.P. Swapna et al. [18]. They fabricated Organically modified halloysite nanotube (HNT) containing polysulfone (PSU) membranes by the wet phase inversion method. They found that the wettability of membranes was found to increase with the weight percentage of HNT in the presence of polyether amine.
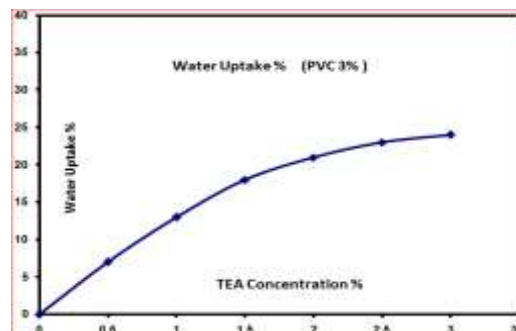

Fig. 3 The influence of different portions of TEA on membranes wettability.

3.3 Surface Roughness

Surface roughness of PVC and PVC-TEA membranes were measured and recorded in Figure 4.It is clear that the roughness increase by increasing the PVC content in the membrane, while the results show decrease in surface roughness of membranes by increasing TEA concentration, due to the interaction between hydrophilic amine (i.e.; TEA) and hydrophobic polymer (i.e.; PVC). The figure also showed the increase of the roughness of membranes at lower surface than that of upper one especially in high concentrations of TEA. This observation could be explained by partially precipitation for TEA from solution during casting, solvent evaporation process and removed in washing step to generate more rough pours surface than the upper one.
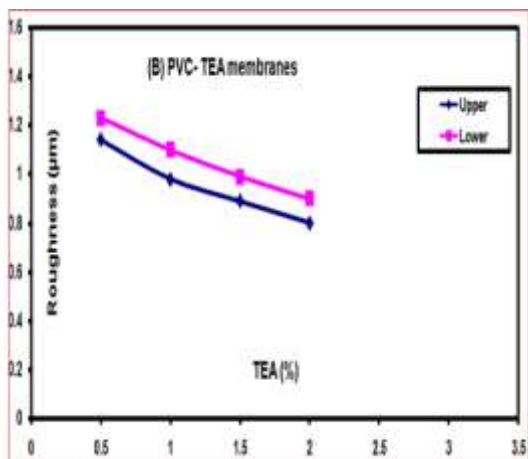

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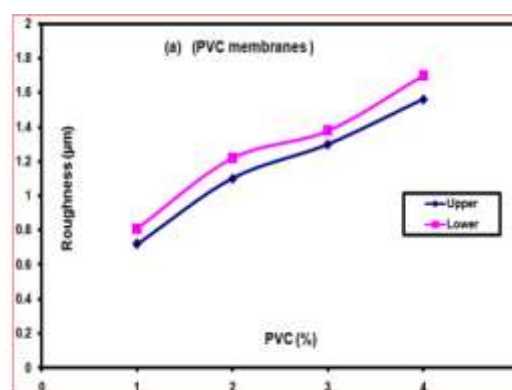
Fig. 4 Effect of a) PVC or b) TEA contents on roughness of membranes.

3.4 Wetability

On the other side, the surface wetability of PVC-TEA membranes was determined using contact angle measurement. Figure 5showed the contact angle values of PVC-TEA membranes in functions with TEA concentrations. The results revealed that the values of membrane surface contact angles significantly decreased with increasing TEA, due to the increase of the hydrophilic characteristics of PVC – TEA membranes. The results are in good view with the work of Thomasukutty Jose et al. [19] in which a series of crosslinked PVA nanocomposite membranes were prepared by varying the concentration of bentonite nano clay and were effectively employed for the PV process. the water contact angle decreases with the addition of hydrophilic bentonite clay to the crosslinked membranes. The decrease in water contact angle with an increase in filler loading indicates that the hydrophilic nature of the nanocomposite membranes increases. Thus, the membranes become more favourable for the separation of water mixture containing organics.
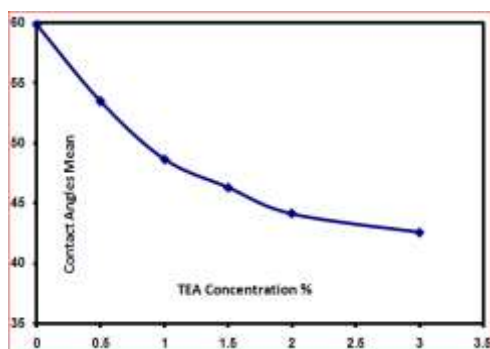

Fig.5 Contact angle of PVC-TEA membranes in functions with TEA concentrations.

3.5 Effect of Pressure on the Salt Rejection Conductivity

The effect of different pressure values on salt rejection (%), conductivity, and permeability (Flux) was explored in figures6 and 7 respectively which revealed that the values of conductivity surface contact angles significantly increased, and salt rejection decreased with gradually increasing of pressure. The results show that there is two competition (1) Lower salts adsorption during the filtration process on membranes surface and (2) higher membrane porosity and macro-voids formation in membranes matrix. Results of permeability flux shown in Fig. 7 are in very good agreement with the water content results (Fig. 3) [20]. In addition, increasing porosity of blend PVC/TEA membranes (which was observed by SEM shown in Figs. 11, 12 respectively) can be shown as another reason for higher permeation flux of blend membranes compared to PVC one.
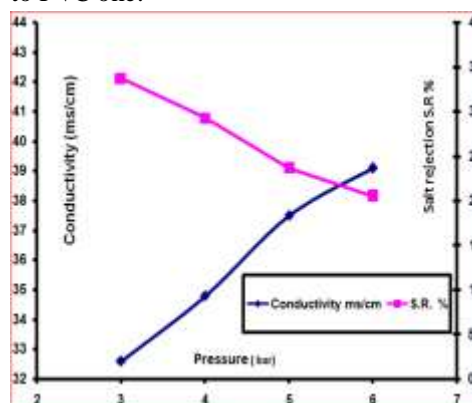

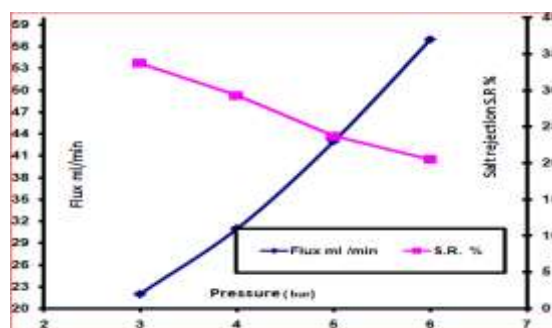Fig.6 Effect of pressure on salt rejection (%), conductivity.

Fig.7 Effect of pressure on salt rejection (%) and permeability

3.6 Characterization

It was expected that the hydrophilicity of the PVC modified membrane surface would be improved by the addition of TEA in the PVC solution. In order to

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verify the existence of additives on the film surface, the surface characterization of PVC and PVC modified membranes was then performed by FT-IR, TGA, and SEM.

3.6.1 FT-IR Spectra of PVC and PVC-TEA membrane

The FT-IR spectra of PVC and modified PVC-TEA membranes are shown in Fig.8. Figure 8b exhibits the FT-IR of PVC membrane, it can be seen that CH_2 deformation with C–H stretching mode was observed at 2933 cm^{-1}, C–Cl stretching mode at 950 cm^{-1}. It is clear from Figure 9 that clear peaks at 3053 ,3225 , 3238, 3304, 3323, 3338,3365 and 3429 cm^{-1} with respect to the intensity values 0.099298, 0.0504, 0.0494, 0.0395, 0.0389, 0.03717, 0.03427and 0.315 respectively due to the presence and interference of amino and OH groups of TEA, where both groups affect each other . Therefore, we find the peaks interference in the range from 3353 cm^{-1} to 3430 cm^{-1}, this range belongs to both groups affected by each other. Also, clear peaks observed and ranging from 2300 to 2800 cm^{-1} due to the methylene groups presence in both PVC and TEA.
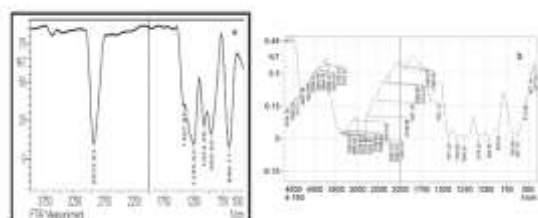

Fig. 8 FTIR of a) PVC b) PVC-TEA membrane films

3.6.2 Thermal gravimetric analysis (TGA)

The thermal degradation of PVC-TEA membrane was conducted using TGA thermal analyzer (Fig.9). The thermal onset decomposition temperature (T_{onset}), the decomposition temperature (T_d) at weight loss (57 %), and the sharp thermal degradation stage were discussed in detail in order to describe the thermal decomposition behavior of PVC-TEA membranes. Results show that the thermal stability of PVC-TEA membranes was improved with the presence of TEA. This phenomenon can be ascribed to the interaction between two moieties of hydrophilic and hydrophobic polymer of TEA and PVC, respectively.
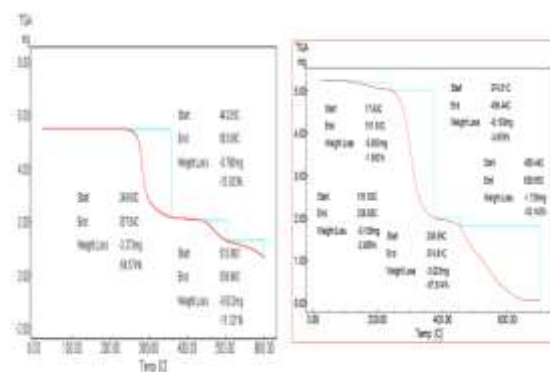

Fig. 9 TGA of a) 3% PVC and b)3% PVC- TEA membranes

3.6.3 Mechanical Properties

Since the tensile strength and the elongation of most membranes are inversely related, it is essential to consider both properties simultaneously to gain the complete view of the mechanical properties of the films. It is ideal to have tough membranes with an optimal tensile strength and percent elongation for their controlled release application. The mechanical properties of PVC membranes with different concentrations of PVC were determined from critical breaking point of stretching pieces. It is shown from Figures 10 that the change happened by the addition of TEA to PVC on density, the tensile strength and maximum force.
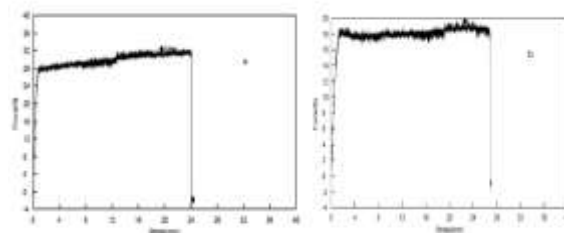

Fig.10 Mechanical properties of a) 3% PVC membrane and b) 3% PVC with 2% TEA membranes.

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The addition of TEA to PVC lowers the viscosity of the PVC membrane solution, where TEA addition causing a decrease in the tensile strength which is in good agreement with Dashuai Zhang et al [21]. In their study, novel physical blending modified membranes are prepared using the non-solvent induced phase separation method, the influences of nano-graphite and PVC incorporated into the hydrophobic performance of the polyvinylidene fluoride (PVDF) membrane were investigated. The surface roughness of the composite membrane is changed, and the hydrophobicity of the composite membrane is enhanced compared with the original PVDF membrane. The mechanical studies show that with increasing nano graphite, the mechanical strength decreases. In our study, it is clearly seen that for 3 % PVC and PVC with TEA, the decreasing takes place on the force from 32 N to 20 N with increasing in stroke from 24 mm to 27 mm, by addition of TEA to PVC. It was found that the hydrophobicity of the composite membranes was improved by adding TEA by changing the surface roughness of the composite membranes. However, the mechanical strength of the composite membranes still needs further study

3.6.4 SEM analysis for PVC and modified PVC membranes

The surface morphology was investigated using SEM. Figures 11 and 12 represent the morphology changes due to addition of TEA to PVC. Presented images show presence of pores and internal channels formation with the presence of TEA as pore forming. After the addition of TEA, the membrane surface becomes more hydrophilic and the affinity between the casting solution and water increases, so the polymer solution will attract more water and the diffusion process of water into the polymer matrix will be faster [22].
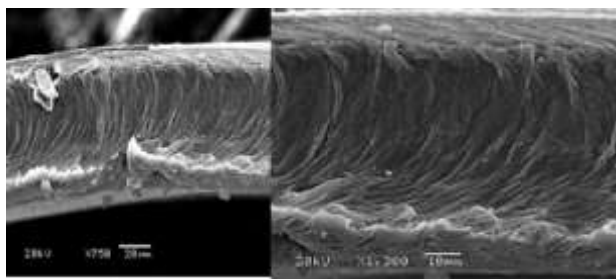
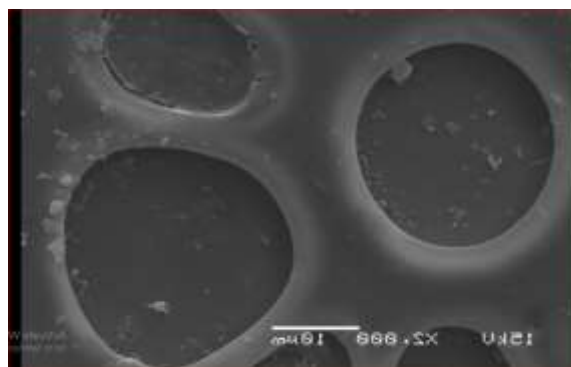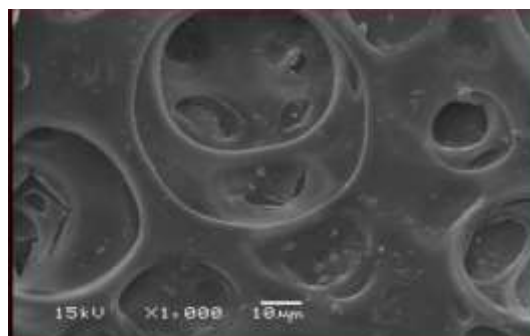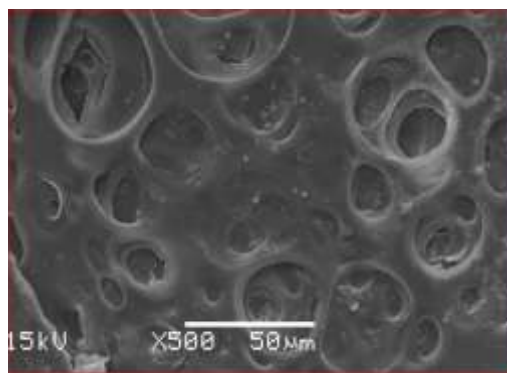
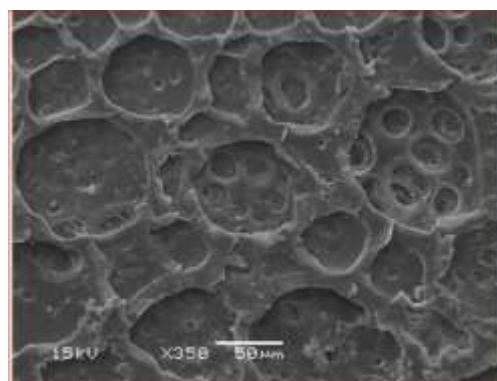
Fig. 11 SEM of surface of (3% PVC).

Fig. 12 SEM of surface of 3% PVC – 2% TEA membrane

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4. Conclusion

From this recent study, it can be concluded that: Morphological analysis using SEM shows the increasing of the membrane porosity after the addition of TEA. The water permeability of PVC membrane increases after addition of TEA. Water permeability and salt rejection are found on the membrane with 2% addition of TEA.it reaches 58ml/min for permeability and 55% for salt rejection. Regarding the water contact angle observation, it is found that the hydrophilicity of the membrane improves as the portion of TEA is increased. Regarding the experimental results, it can be concluded that TEA succeeded in improving hydrophilic properties, filtration performance, and maintaining the stability of the membrane. Thus, the TEA is useful to be applied in the water treatment industry.

3. Conflicts of interest

There are no conflicts to declare".

4. Formatting of funding sources

There are no funding sources for this paper.

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