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Development of membrane blend using casting technique for water desalination

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Abstract. Membrane separation technologies have some of advantages are considered a better alternative to traditional methods. Research of novel membranes is very vital for covering the higher required of membrane in several purposes like water desalting technology. In this work polyamide-6/ cellulose acetate (PA-6/CA) blend membrane was developed according to the wet phase inversion system. The structures of the prepared membranes were examined by scanning electron microscopy (SEM). SEM images showed uniform particles distribution in the prepared membranes. Moreover, SEM images revealed that the membranes have relatively uniform surface (PA-6/CA). PA-6/CA blend membranes systems are evaluated by using synthetic NaCl solution. The separation performance showed that salt rejection increased with increasing of heat treatment of the casted films and it was improved with increasing of operating pressure.

Keywords: membrane blend; casting; desalination; polyamide; cellulose acetate

1. Introduction

Recently, the development of novel membranes is becoming a vital issue for covering the higher required of membrane in several purposes such as water technology. Thus, several researches are concerning that issue with investigation number of methods such as blending, coating, grafting, and surface treatment (Yao *et al*. 1987, Shashidhara *et al*. 2002, Ani *et al*. 2008, Haack *et al*. 2000, Idris *et al*. 2006, Ramrez *et al*. 2006, Pham*et al*. 1999, Ani *et al*. 2007, Sivakumar *et al*. 2006, Wang *et al*. 2005, Chen *et al*. 1999, Chen *et al*. 1998, Mark *et al*. 1990, Ghosh *et al*. 2011).

Fortunately, blending process involves of obtaining new structural materials with an extremely attractive and inexpensive. Blending polymers is one of the available methods which probes their individual superior properties in the final mixture while concurrently reduces their poor characteristics (Chitrakar *et al*. 2012, Lau *et al*. 2010). Generally, some of researchers investigated blending process for membrane polymers materials such as CA/poly-ether-sulfone (PES), CA/ carboxylated, CA/polyurethane, CA/PSf, etc. for membrane formation and their properties (Yu *et al*. 2006, Arthanareeswaran *et al*. 2010, Mahendran *et al*. 2004). These blended membranes have improved permeability, hydrophilicity, and chlorine resistance, and are used for membrane separation applications (Sajith *et al*. 2002).

In fact, nylon polymers are available, moreover that polymers are less micro-organism susceptible and are more stable over a wider range of pH values, suitable for more aggressive cleaning,

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chemical resistances and good mechanical strength (Shashidhara *et al*. 2002, Takuji *et al*. 2009, Jochen *et al*. 2004, Yao *et al*. 1987). Therefore, the modification of polyamide has gained importance.

On the other hand, Cellulose acetate (CA) is one of the first polymers that have been used for membrane water desalination (Arthanareeswaran *et al*. 2006). Cellulose acetate (CA) has always promising characteristics such as good toughness, high bio-compatibility and excellent hydrophilicity that is very important in minimizing fouling, providing good desalting, characteristics, and high potential flux and relatively low cost. However, cellulose acetate is not suitable for more aggressive cleaning, has low oxidation and chemical resistances and moderate mechanical strength (Idris *et al*. 2006, Ehsan *et al*. 2009, Ahmed *et al*. 2010).

Hence, this work aimed to evaluate the performance of PA-6 membrane for water desalination via NF/RO system. We attempt to develop a (PA-6/CA) blend membrane to improve separation and to increase the hydrophilicity of the polyamide-6.The effect of preparation conditions of the casting process as heat treatment on the performance of membrane was studied.

In our previous work, PA-6 membranes were developed to separate of para-nitro phenol (PNP) from aqueous water mixture (El-Gendi *et al*. 2007, El-Gendi *et al*. 2005). The ultimate objective of this work was to prepare a suitable RO/NFmembrane for water desalting. As a part of the problems of desalting using homogenous PA-6 membrane, we have studied from a fundamental point of view, how it was possible to develop a novel asymmetric PA-6/CA blend membrane via casting method, and to achieve separation of saline water by RO/NF system.

2. Experimental

The experimental program adapted for preparation of PA-6/CA membrane by casting process to investigate the parameters affecting the preparation process, membrane characterization and performance of the casted membrane are outline below.

2.1 Material

The following Chemicals have been used: Polyamide-6 (PA-6) with bulk density 0.25 gm/ml and particle size 50-160 μm (Fulka Company Switherland); Formic acid (FA) with average MW: 46.026 g/mol, density: 1.198 gm/cm^3 at 20°C and 100.7°C boiling point (El-Naser pharmaceutical Chemicals Company, Egypt); and cellulose acetate with acetyl content of 39.8 (Acros Organic company, New Jersy, USA Germany).

2.2 Membrane preparation

Membrane preparation steps as presented in Fig. 1 include the preparation of casting solution using PA-6/CA (20) wt. % (PA-6: CA= 4:1) and formic acid (80) wt. %.

The casting solutions are then casted into a glass plates by using doctor blade with drawdown thickness up to 200 μm for 1 minute. The casted films are immersed into a coagulating bath containing pure water at temperature 18°C for 60 minute. The glass plates are then immersed into washing bath containing pure water at temperature 25°C. The flat sheet membrane formed is stripped from the carrier, and then the prepared sheet passed by a thermal treatment at temperature ranged from 25, 80, 90,100 and 120°C then it is stored in a distilled water bath until it is used.

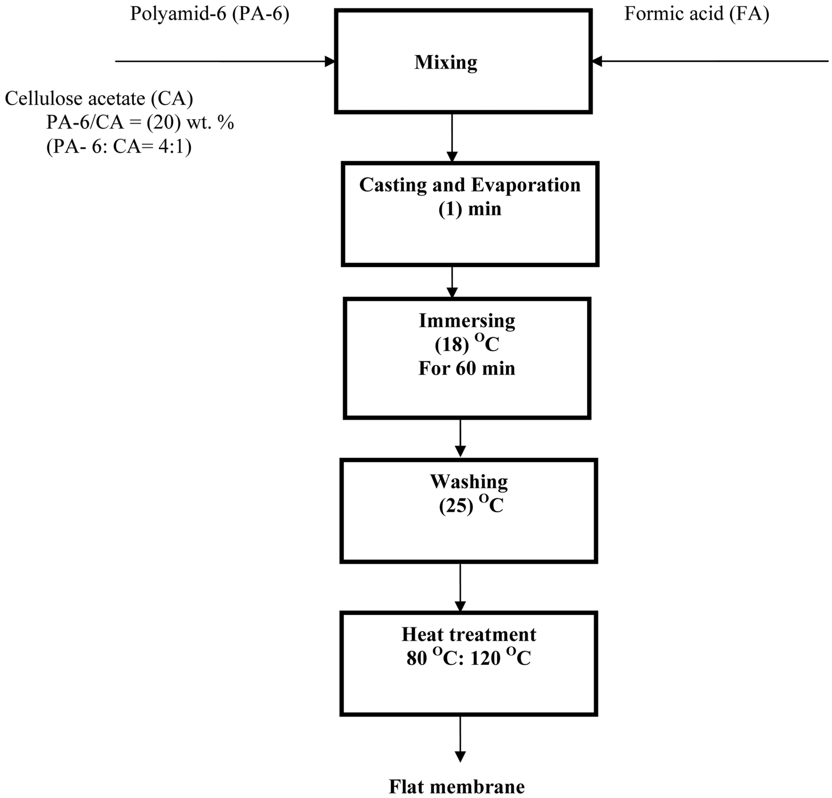

Fig. 1 Process flow diagram for preparation of PA-6/CA membrane

2.3 Membrane characterization

2.3.1 Membrane morphology

Scanning electron microscopy (SEM) was used to examine the morphology of PA6/CA casted membranes; however samples of membranes were coated with gold to provide electrical conductivity. After that these membranes were performed on Scanning Electron Microscopy of Model JEOL-JXA-840 A, and were applied at different kV with magnification 10x up to 400,000x

2.3.2 Membrane mechanical properties

Membranes which give the best performance were subjected to heat treatment at temperature of 25, 80,100 and 120°C. The tensile strength and elongation % of these membranes were measured using mechanical testing apparatus INSTRON-5500R, the gauge length and width of dumb bell tensile specimens were 6.2 and 0.16 mm respectively.

2.3.3 Osmotic pressure (P_{osm})

The osmotic pressure (P_{osm}) of a mixture solution is calculated by the following equation (Mark *et al*. 2007)

$$P_{osm} = R\,(T+273)\Sigma(mi) \qquad (1)$$

Where P_{osm} is osmotic pressure in bar, R is the universal gas constant (0.082 L*atm/mol ^oK), T is the temperature in ^oC, and Σ(mi) is the sum of molar concentration (molarity) of all constituents in a solution.

2.4 Membrane performance

Evaluations of membrane performances as a function of different operating parameters have been investigated. The prepared membrane sheets have been tested to check their mechanical strength under different applied pressures.The permeation tests were carried out at ambient temperature under an operating pressure up to 45 bar; the feed solution has capacity of 20 L. The effective surface membrane area of 19.7 cm^2. The total flux (J) of the tested solution was determined from equation

$$\mathbf{J} = Q/\ (A*Tt) \tag{2}$$

Where; Q: permeate mass in kg, A: membrane active area in m^2, Tt: time in hour
Where the rejection (R) was calculated as

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

where; C_f : the concentration of the feed solution, C_p: the concentration of the permeate
The concentrations of C_p and C_f were measured with the conductivity meter (walk lab). In addition, the concentration of saline in the feed solution was 2.5:4.5 g/L. The testing set up system is presented elsewhere (El-Gendi *et al*. 2007, El-Gendi *et al*. 2005).

3. Results and discussions

3.1 Membrane preparation

Membranes tobe suitable in a suchseparation processes should have good mechanical resistance, high chemical resistance (compatibility), thermal stability, sorption capacity, and good mechanical strength in the solution required to withstand filtration processing conditions. In addition, the developed membranes need to be stable in terms of permeability and selectivity under standard operating conditions for extended periods.

3.2 Membrane characteristics

3.2.1 Membrane morphology (SEM)

SEM photographs show that constitutionally different features in the combinations of the two polymers leads to different membrane morphologies for different composition of casting solution. Prepared membranes have been shown in Fig. 2.

SEM photographs show that, there is a completely difference in the surface morphology, with increasing heat treatment of the prepared polymer blend PA6/ CA from 25 to 120^oC. The PA-6 membranes under investigation were prepared by the phase inversion process. By this special preparation method membranes with an asymmetric structure consisting of a thin top layer and a highly porous sublayer are obtained. The separation process takes mainly place in the top layer whereas the sub-layer acts as a mechanical support.

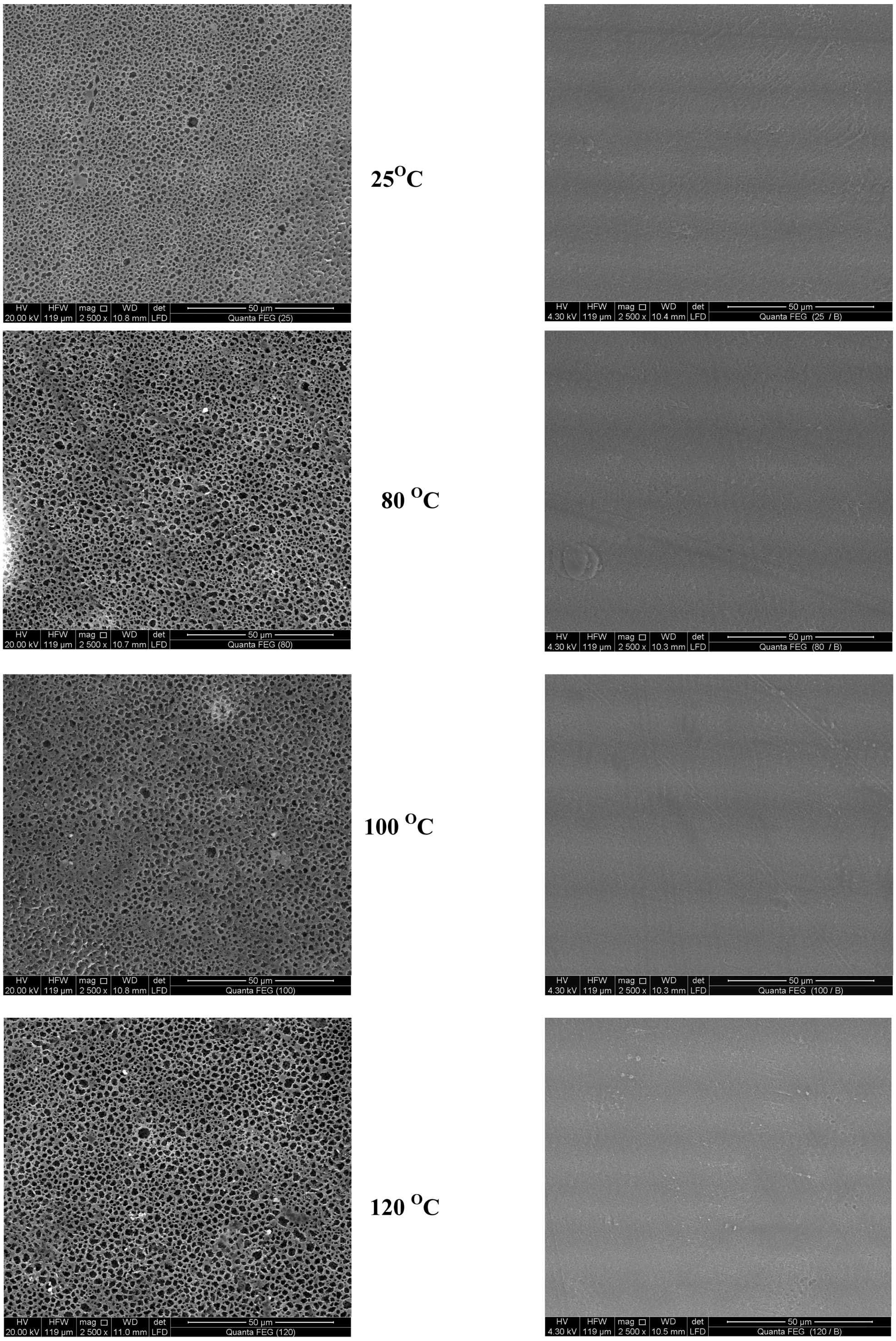

Fig. 2 Effect of thermal treatment on PA6/ CA polymer blend at temperature of 25, 80,100 & 120 where *Left* is the bottom and right is the top respectively

Table 1 Mechanical properties of prepared PA_6/CA blend membrane

Annealing temperature °C	Tensile strength (Kg/cm^2)	Elongation %
25	556.291	24
80	635.762	10
100	829.474	12
110	683.20	10.5
120	543.046	9

Fig. 2 shows the morphology of the top surface and the bottom surface, respectively at temperature of 25, 80, 100 & 120°C. The top surface consists of nonporous dense structure or very fine surface. The bottom surface exhibits a highly homogenous porous structure.

3.2.2 Mechanical properties

Tensile strength, elongation at constant thickness of 100 μm of the prepared PA6/CA blend membranes which were subjected to heat treatment have been investigated to indicate the effect of various annealing temperature (25, 80, 100, 110 & 120°C) on the prepared blend membrane properties and to determine the appropriate annealing temperature which can be used without affecting the membrane strength. Table 1 shows that the maximum tensile strength is 829.5 Kg/cm^2 with elongation 12% at annealing temperature 100°C. The further increasing in annealing temperature can lead to more shrinkage of the pore structure for the blend membrane which leads to decreasing in water flux.

3.3 Membrane performance

The membrane performance of asymmetric PA-6/CA membranes was reported to determine the most suitable membranes. Rejection experiments of saline solution with the asymmetric PA-6/CA membrane sheets have been carried out at different operating pressures in order to evaluate their performances. The results have been summarized in the following section.

3.3.1 Effect of thermal treatment temperatureon membrane performance

The effect of thermal treatment temperature on the casted PA-6/CA blend membranes (M_{1-80}, M_{2-90}, M_{3-100}; at 80, 90, 100°C respectively) were studied with saline solution contains 4500 mg/L NaCl at 20 bar. The results were presented in Table 2.

It was obvious from Table 2 that the salt rejection increased with increasing of heat treatment where the permeate flux was decreased. It may be explained that the higher is thermal treatment temperature, the denser is the active layer and the closer is the pore distribution like M_{3-100} which showed the best rejection.

Table 2 Performance of the prepared membranes at 20 bar, feed 4500 mg/L NaCl

Membrane	Flux (kg/hr.m^2)	Rejection %	The osmotic pressure (P_{osm}) (bar)	Thickness μm
M_{1-80}	248	9	1.89	100
M_{2-90}	14-15.5	29-20	1.89	100
M_{3-100}	8	45	1.89	100

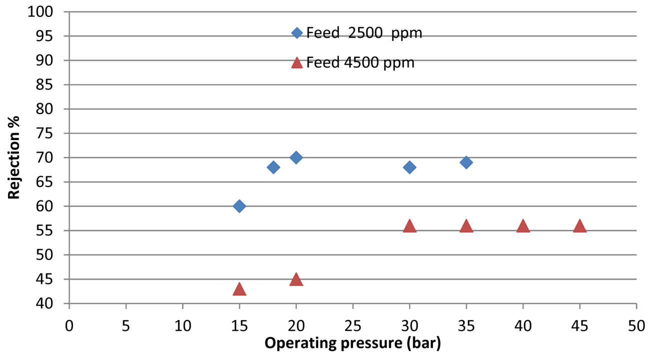

Fig. 3 Effect of operating pressure on rejection of $M_{3\text{-}100}$ (Feed; 2500 and 4500 ppm NaCl)

3.3.2 Effect of operating pressure on rejection

The membrane performance was determined for all prepared membranes using 2.5:4.5 g/L NaCl synthetic solution. Influence of operating pressure on rejection was investigated using asymmetric PA-6/CA membranes. The observed rejection is plotted against applied pressure for feed solutions.

It was found out that the rejection was decreased with increasing of feed salt concentration as shown in Fig. 3. The decrease in salt rejection with increasing salt concentration is consistent with the Donnan exclusion model (Wang *et al*. 2008). Our results is in agreement with Fraeger *et al*. (2000) who studied nanofiltration (NF) of aqueous inorganic mixtures using the FILMTEC™ NF-200B aromatic polyamide membrane, and reported rejection of 4% NaCl, 9% NaCl are 36%, 25% respectively.

Fig. 3 Showed that the salt rejection with the asymmetric PA-6/CA blend membranes increased with an increase of applied pressure start from 15 up to 20 bar while it was stable from 20 to 45 bar; this mean that the prepared membrane is a low pressure reverse osmosis membrane.

3.3.3 Effect of operating pressure on permeate flux

Influence of operating pressure on permeate flux was investigated using asymmetric PA-6/CA membranes.The observed flux (J) is plotted against applied pressure for feed solutions.

Fig. 4 showed that the flux of asymmetric PA-6/CA membranes increased with an increase of applied pressure. This confirms that all membranes follow Darcy’s law. Further, the permeate flux for pure

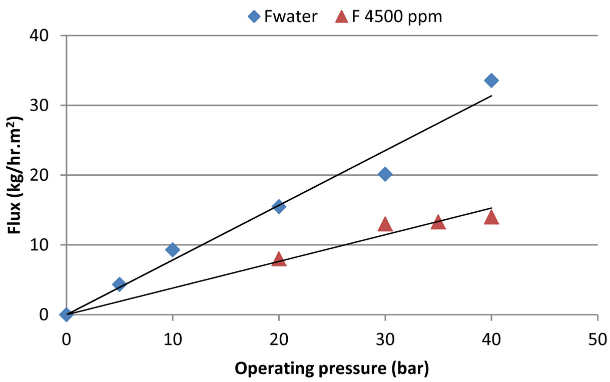

Fig. 4 Effect of operating pressure on flux of $M_{3\text{-}100}$ (Feed; pure water, 4500 ppm NaCl)

water is better than the saline solutions. Thus, it is clear that the saline solution has an influence on decreasing the flux. This type of result is not surprising and has been observed previously by other studies (Mark *et al*. 2007, Yoon *et al*. 2005, Zhou *et al*. 2009, Jarusutthirak *et al*. 2007).

Mark (2007) reported that the solvent passes through the membrane at a faster rate than the passage of dissolved salts in solution. Hence, the difference of passage rate results in solvent-salts separation.

4. Conclusions

PA-6/CA blend membranes have been successfully prepared via casting technique.The developed PA-6/CA blend membranes are characterised via both the membrane performance and SEM inspection. The results indicated that, the permeate flux decrease with increasing of annealing temperature due to densification of membrane morphology while it was increased with increasing of operating pressure. However, the increasing in annealing temperature means decreasing in the pores size of membrane and more densification of the thin film membrane and it's active layer. Salt rejection increased with increasing of annealing temperature and improved with increasing of operating pressure. Generally, annealing process for asymmetric PA-6/CA membrane is an essential step which was used to adjust pores size and to improve selectivity of membrane.

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