Modified Nanoporous Asymmetric Polyacrylonitrile Membranes with Merpol as a Hydrophilic Surfactant: Insulin Separation

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Polyacrylonitrile (PAN) membranes are broadly applied in many chemical engineering fields. In this research, asymmetric polyacrylonitrile membranes with high hydrophilicity and permeability were prepared from PAN/merpol/NMP system *via* immersion precipitation. Pure water was used as gelatin media. The effect of variation of polyacrylonitrile molecular weight and addition of merpol on morphology, wet ability, pure water permeation flux and insulin rejection of the prepared membranes were studied by scanning electron microscopy, contact angle measuring instrument and experimental set up. The results demonstrated that both hydrophilicity and permeability of the prepared membranes were significantly enhanced by small additions of merpol surfactant in the casting solution. It was also found out that decrease in the polyacrylonitrile molecular weight results in the formation of membranes with high permeability and sub-layer porosity.

Keywords: Polymeric membranes, Membrane preparation, Phase inversion, Polyacrylonitrile, Hydrophilicity.

INTRODUCTION

In view of the demand for more versatile and highly tailored membranes, membrane technology currently employs a wide range of polymeric materials. Continual development of new membrane materials is crucial to sustain and expand the growing interest in this technology and modern polymer chemistry is highly proficient in tailoring polymers to specific aims in terms of mechanical, thermal and chemical stability [1,2]. The phase inversion process induced by immersion precipitation is a well known technique for preparing asymmetric polymeric membranes [3-10]. In this technique, an appropriate polymer solution is spread across a flat plate with a casting knife. After casting, the solution is immersed into the coagulation bath (precipitation media), where the solvent is exchanged with the non-solvent and phase separation takes place. In phase separation process, the liquid polymer solution is precipitated into two phases: a solid, polymer-rich phase that forms the matrix of the membrane and a liquid, polymer-poor phase that forms the membrane pore. This process results in an asymmetric membrane which consists of an extremely thin surface layer supported on a much thicker, porous substructure. To attain the desired membrane morphology and performance, the phase inversion process must be carefully controlled [5,9,11]. Two influential factors controlling the formation of phase inversion membranes are thermodynamics and kinetics, the former is related to the phase equilibrium between components in the coagulation bath and the later is related to the mutual diffusivities between them.

Polyacrylonitrile (PAN) is one of the versatile polymers that are widely used for making membranes [12]. Polyacrylonitrile has been used as a substrate for ultra filtration (UF), nanofiltration (NF) and reverse osmosis (RO) membranes [13]. This polymer exhibits good solubility in different solvents such as N,N-dimethylacetamide (DMAc), N-methyl-2-pyrrolidone (NMP), N,N-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) [14,15]. Among four solvents used for the dope solution preparation, NMP was found to offer membranes with optimal combination of flux and rejection of various solutes [16]. Different post treatment techniques such as chemical and plasma modification [17,18], graft polymerization [19-21], the chemical conversions of the nitrile groups [22,23], photo-initiation [24,25] and ion-beam irradiation [26] can be used for the production of modified PAN membranes. These techniques can improve permeation behaviour and hydrophilicity of the prepared membranes. Higher hydrophilicity of modified PAN membranes can result in increasing the flux and life of them as well as decreasing the operating costs [27-56].

Above modification methods suffer the drawbacks of requiring additional complicated steps. However a promising *in situ* modification of the hydrophobic membranes can be obtained by addition of hydrophilic additives to the membrane casting solutions. It seems that the addition of surfactant additives, with a hydrophilic head and hydrophobic tail, can influence topology and performance of the membranes. There is no previous published article with relation to the effects of addition of merpol surfactant as hydrophilic additives for the improvement property of the PAN membranes.

In the present work we carried out the fabrication of high flux polyacrylonitrile (PAN) membrane by phase inversion method with NMP as solvent and merpol as additive. Distilled water used as coagulation bath. The effects of merpol additive and polymer molecular weight on morphology, hydrophilicity, pure water permeation flux (PWF) and insulin rejection of the PAN membranes were investigated in details. Merpol is a non-ionic, polyethylene oxide surfactant used as a wetting and emulsifying agent to achieve better fabric permeation.

EXPERIMENTAL

Polyacrylonitrile with average molecular weight of 150,000 g mol^{-1} (Aldrich, USA) and 70,000 g mol^{-1} (polyacryl) were used as the membrane-forming polymers. 1-Methyl-2-pyrrolidone (NMP) with an analytical purity of 99.5 % and distilled water were used as the solvent and the non-solvent agents, respectively. "MERPOL HCS" Surfactant with HLB = 15 (Aldrich, USA) was used as a nonionic surfactant additive in the casting solution. Also, insulin (m.w. = 5700 g mol^{-1}), obtained from Wishwani, India, was used as protein in preparation of the model solution.

The asymmetric PAN membranes were prepared using different casting solutions of PAN, merpol and NMP by the phase inversion process. Compositions of solutions are presented in Table-1. After solving merpol in NMP, PAN was gradually added to the solution. Then the solution was stirred continuously and heated in regular time intervals to ensure that the polymer was completely dissolved. By observing a clear solution which indicates the polymer is completely dissolved, the solutions remained overnight before casting to remove air bubbles. The prepared homogeneous solutions were cast using a casting knife with 300 μm clearance gap on a glass plate substrate. Then, the glass plate was immediately immersed in a distilled water coagulation bath for immersion precipitation. After primarily phase separation and formation, the membrane was stored in water for 24 h to guarantee complete phase separation. This allows the water soluble components in the membrane to be leached out. Afterwards the membranes were put under pressure between two filter papers for drying.

TABLE-1
COMPOSITION OF THE CASTING SOLUTIONS

Membrane	PAN (wt. %)	Molecular weight of PAN (g/mol)	Merpol (wt. %)
M1	12	150,000	0
M2	12	150,000	2
M3	12	150,000	4
M4	12	150,000	6
M5	12	150,000	8
M6	12	70,000	8

RESULTS AND DISCUSSION

The permeation flux studies were carried out using a batch adsorption mode. A flat sheet membrane module made from stainless steel was used in all experiments. The effective area of the membrane in the module was 20 cm^2. The schematic representation of set-up is shown in Fig. 1. The PWF measurement was carried out in a membrane pressure of 1 MPa.
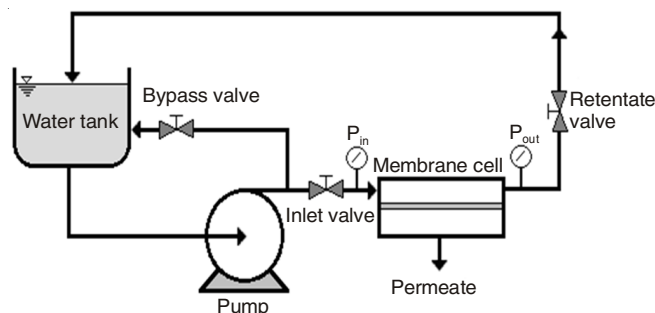

Fig. 1. Schematic diagram of the experimental setup

Pure water permeation flux was calculated using the following equation:

$$\text{Flux} = \frac{Q}{A \Delta t} \tag{1}$$

where Q is the quantity of permeate (L), A is the effective membrane area (m^2) and Δt is the sampling time (h).

The performance of the prepared membranes was characterized using a cross-flow system. The synthesized PAN membranes were housed in the cross-flow cell. The protein, insulin, was dissolved (0.1 wt. %) in phosphate buffer (0.05 M, pH 7.2) solution. All the experiments were conducted under feed pressure of 5 bar. Percentage rejection of insulin was calculated using the following equation:

$$R\ (\%) = 1 - \frac{C_p}{C_f} \times 100 \tag{2}$$

where C_p and C_f are protein concentration in permeate and feed streams, respectively. Samples were taken from the permeate and the retentive streams to determine their protein concentrations using UV-visible (Unico UV-2100, Midsci, St. Louis, MO, USA) at 280 nm.

SEM images taken from cross section of the prepared PAN membranes using different amounts of merpol as surfactant (Fig. 2). Before adding merpol, the membranes contain a dense top layer and a very low porous support layer, whereas adding merpol to the casting solution incites macro voids formation resulting in increase of porosity. The prepared membranes possess asymmetrical structure consisting of a dense top layer and a porous sub layer with finger-like macro voids.

The SEM (Model XL-30, Philips, Netherlands), for this purpose the membrane samples were fractured in liquid nitrogen and then coated with gold under vacuum conditions. The morphology of the top-layer (fractured in liquid nitrogen) of the membrane were examined with a field emission scanning electron microscope (Hitachi S4160, Japan). The SEM images indicate that these macro voids are formed with adding little amounts of merpol (up to 6 Wt. %) to the casting solution, but
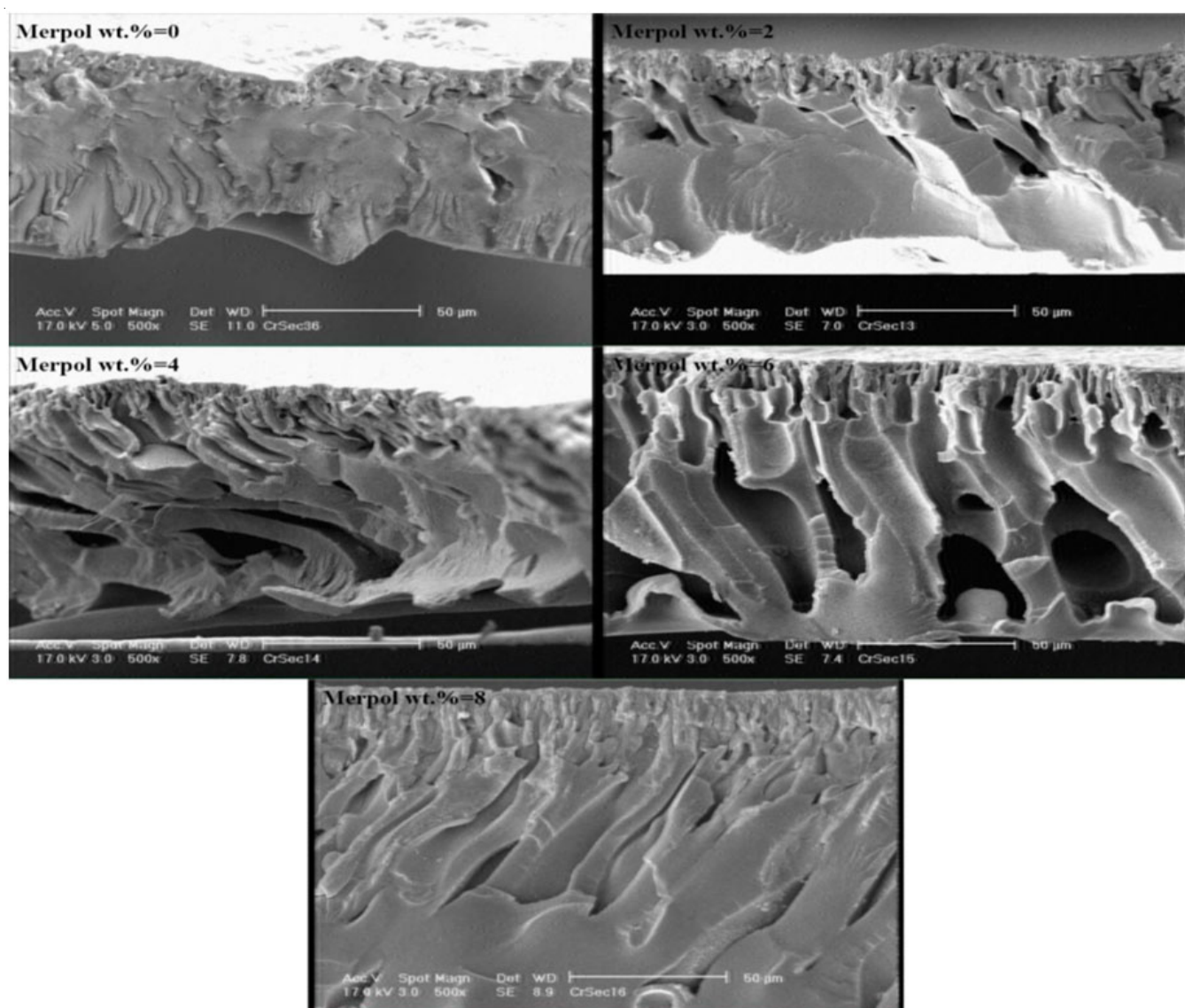
Fig. 2. Variation effect of merpol concentration on the cross-sectional images of the PAN membranes (500X magnification)

more addition of merpol leads to dense structure of the sub layer. This phenomenon can be referred to two contrasting effects of merpol on the casting solution. On the one hand, low miscibility between additive and polymer intensifies thermodynamic instability of the immersed film and conse-quently, causes instantaneous demixing in the coagulation bath which facilitates formation of macro voids. On the other hand, the presence of additive increases the viscosity of the cast film. Increase of the viscosity of the cast film prevents the fast exchange of solvent (NMP) and non-solvent (water) during phase inversion process which consequently leads to delayed demixing [57]. During the phase inversion process, the rate of demixing plays a significant role in membrane formation controlling the resulting membrane morphology. Instantaneous demixing often leads to the formation of macro voids in the membrane structure, whereas slow demixing results in a denser structure [4]. Hence, final structure of membranes depends on which effect will overcome. In this study, increase of merpol up to 6 wt. %, caused intensification of thermodynamic instability and hence, instantaneous demixing which results in more porosity. However, it seems that in the higher concentration

of merpol (8 wt. %), viscosity effect has overcome thermodynamic instability leading to suppression of macro voids formation and hence, a denser sub layer in membranes is formed.

Fig. 3 shows FESEM images of PAN membranes surface morphologies. As demonstrated in the FESEM images, by adding merpol to the casting solution, the surface of the prepared membranes becomes denser and the mean pore size at the top-surface reduces. A more increase of merpol concen-tration leads to more decrease in the size of pores. This change in the pore size can be explained as a result of interactions among the components in the casting solution as well as phase inversion kinetics. The more amount of merpol in the solution increases, the more viscous solution is formed which leads in prevention of the diffusion exchange between solvent (NMP) of the film and non-solvent (water). Consequently, a higher concentration of the polymer is made at the interface between the polymer film and non-solvent. This leads to the formation of a membrane with smaller pore size on the top surface. Membranes prepared from the casting solution, resulted compact surfaces with small surface pore sizes. In fact, the pore sizes on top layer of membranes are commonly in the

size of nanometer. It is difficult to see the pore structure of membrane surface using scanning electron microscopy.

The effect of variation in molecular weight of PAN with two levels (70,000 g/mol and 150,000 g/mol) on cross section morphology is shown in Fig. 4. As it can be seen in Fig. 4, reduction of molecular weight of the polymer in cast solution leads in macrovoids formation so that voids extend in whole of the membrane support layer from top to bottom.

In fact, reduction of molecular weight of the polymer results in reduction of viscosity and resistance against the mutual diffusivity between the solvent (NMP) and nonsolvent (water) during solidification of the casting solution in the coagulation bath which facilitates coagulation process and membrane formation.

FESEM images (Fig. 5) taken from the upper surface of prepared membrane with different molecular weights of PAN in cast solution, indicate clearly that the membrane pore size decreases with increase of molecular weight of the polymer in a constant concentration of the polymer and the additive.

The contact angle between water and the membranes was directly measured using a contact angle measuring instrument (OCA15plus, Data Physics, Filderstadt, Germany) for the membranes hydrophilicity evaluation. Drops of distilled water were deposited onto the membrane surface and the direct microscopic measurement of the contact angles was done with the goniometer. Contact angles were measured to evaluate the changes in the hydrophilicity and surface properties of the PAN membranes after blending with the merpol and variation in molecular weight of PAN.

Table-2 shows the effect of variation in molecular weight of PAN and addition of merpol, as a hydrophilic surfactant, on the contact angle and wettability of the PAN membranes. As shown in Table-2, the highest contact angle (75°) and in other words the lowest hydrophilicity, is obtained for the PAN membrane without addition of merpol in the casting solution (M1). However, addition of hydrophilic merpol resulted in reduction of contact angle and in other words, formation of membranes with higher hydrophilicity. For instance, maximum addition of hydrophilic merpol (8 wt. %) resulted in the lowest contact angle (42°) and in the other words the highest hydrophilicity.

The above reduction of contact angle from 75 to 42° can be attributed to and explained by amphiphilic property of the merpol. In other words, this surfactant comprises hydrophilic head and hydrophobic tail. Hydrophilic head facilitates transmission of merpol to the surface of the casting film after immersion into the coagulation bath. On the other hand, organic chains in hydrophobic tail of merpol and their interaction with the polymeric chains is an important resistance against the coming out of merpol to the coagulation bath (Fig. 6). Thus amphiphilic property of merpol results in its accumulation near the surface of the cast film and consequently formation of membrane with noticeable hydrophilicity [58].

The pure water flux of PAN membranes prepared of different concentration of merpol is shown in Table-2. It can be seen that PWF of the PAN membranes, initially, increased by increasing the merpol concentration. However, more addition of merpol (from 6 to 8 wt. %) leads to decreasing the
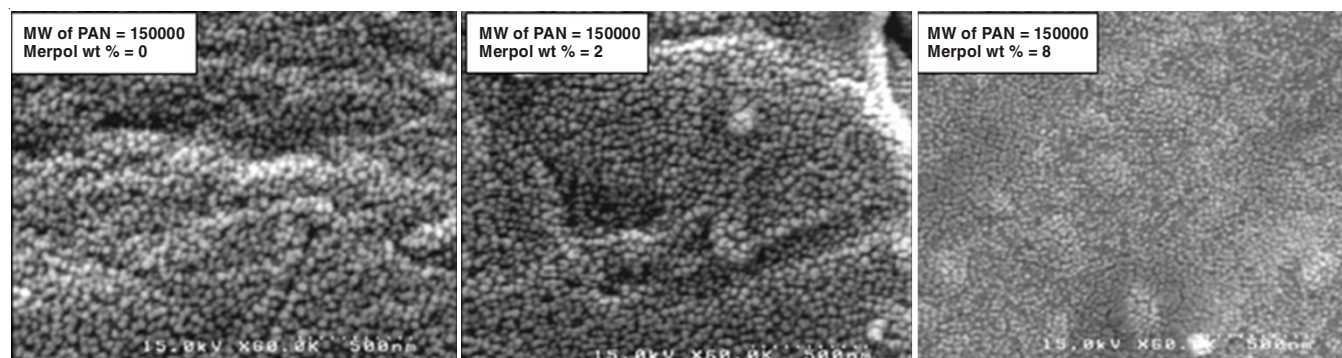

Fig. 3. Effect of varying the concentration of merpol on the top surfaces of PAN membranes
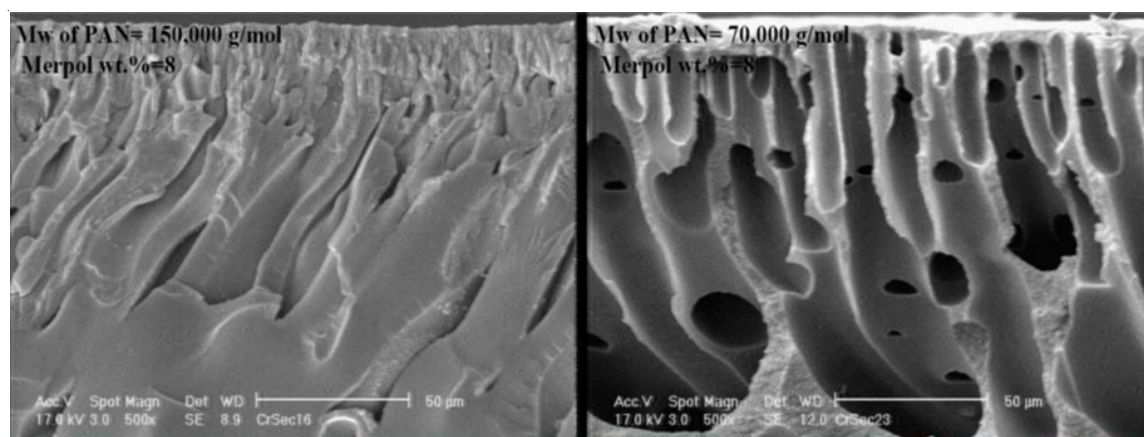

Fig. 4. Variation effect of PAN molecular weight on the cross-sectional images of the PAN membranes (500X magnification)
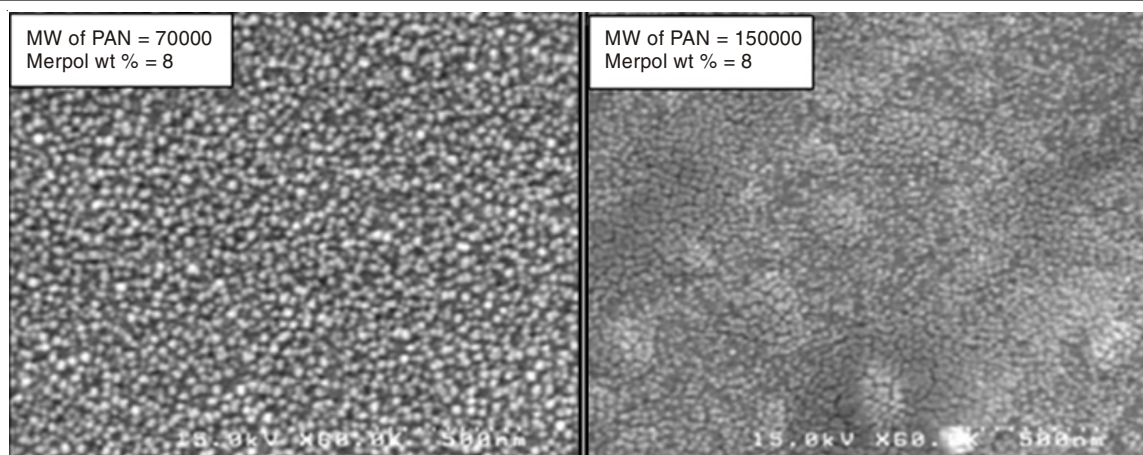
Fig. 5. Variation effect of PAN molecular weight on the top surfaces of PAN membranes

TABLE-2
EFFECT OF MERPOL CONCENTRATIONS AND MOLECULAR WEIGHT OF PAN ON THE
HYDROPHILICITY, PWF AND INSULIN REJECTION OF THE PREPARED MEMBRANES

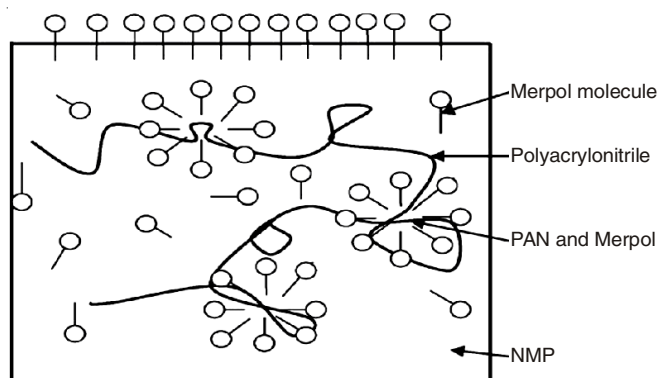| Membrane	Concentration of PAN (wt. %)	Molecular weight of PAN (g/mol)	Concentration of merpol (wt. %)	Contact angle (°)	Insulin rejection (%)	PWF (L/m²h)
M1	12	150,000	0	75	80	198
M2	12	150,000	2	63	86	227
M3	12	150,000	4	59	90	288
M4	12	150,000	6	53	94	322
M5	12	150,000	8	42	97	252
M6	12	70,000	8	41	89	341

Fig. 6. Effect of merpol on the formation of PAN membrane by phase inversion

PWF. This phenomenon can be explained by morphology and hydrophilicity changes in presence of different concentration of merpol. Hydrophilicity of the PAN membranes increased by addition of merpol to the casting solutions (Table-2). Increasing hydrophilicity causes the formation of hydrophilic channels that increase rate of water permeation. Also, addition of merpol (2, 4 and 6 wt. %) to the casting solutions results in formation of macro voids and thus favours higher water permeability by reduction of the main resistance against the water permeation.

According to Table-2, more increase in merpol concentration from 6 to 8 wt. % results in PWF decreasing from 322 to 252 L/m²h. This change in water permeability could be explained by considering SEM images. As observed, further increase in the merpol concentration from 6 to 8 wt. % to the casting solution resulted in suppression of macrovoids and formation of denser structure, leading to lower flux. Also,

higher PWF of M6, 341 L/m²h, in comparison with M5, 252 L/m²h, can be attributed to higher molecular weight of PAN which has been used for preparation of M5, 150,000 g/mol, compared with molecular weight of PAN which has been used for preparation of M6, 70,000 g/mol, results in formation of denser structure (Fig. 4) and consequently PWF reduces.

In Table-2, the protein rejection of the membranes is presented as functions of the merpol concentration and molecular weight of PAN. As observed, membrane without addition of merpol in the casting solution shows the lowest rejection of insulin (80 % for M1). However, membrane prepared by higher molecular weight of polymer (PAN 150,000 g/mol) and maximum content of surfactant (8 wt. %) resulted in the highest rejection of insulin (97 % for M5). In fact and according to Table-2, membranes with higher hydrophilic property, that contain merpol additive or have been prepared by higher molecular weight of polymer, result in higher rejection of insulin. As discussed, increase in molecular weight of polymer and the merpol concentration from 6 to 8 wt. %, result in formation of denser structure and provide higher resistance against the water permeation. Also, the mentioned variation in molecular weight of polymer and merpol concentration results in higher rejection of insulin. According to Table-2, the increase in merpol concentration up to 6 wt. % results in simultaneous increase in the water permeation and insulin rejection that are not compatible with the commonly observed cases that water flux and solute rejection have reverse trends [59,60]. But it should be noted that simultaneous increase in the water permeation and solute rejection is not a rare phenomenon and sometimes both water flux and rejection increase simultaneously [30].

According to Fig. 2, the membrane without merpol additive is too dense. In this membrane, resistance against the feed permeation, for both water and insulin, is noticeable. According to the SEM and FE-SEM images, increasing merpol concentration up to 6 wt. % causes the formation of more porous structures with a dense top layer. As shown in the FE-SEM images, by adding merpol to the casting solution, mean pore size at the top-surface of the prepared membranes reduces.

These changes in the membrane structure by adding merpol may be the major factor in the different behaviour of the membranes in comparison with common cases. As mentioned before, formation of more porous structure along with more hydrophilicity facilitate water and insulin flow through the membrane. However, due to formation a dense top layer with smaller pore size on the membrane surface, caused by adding merpol, insulin components aren't able to pass thorough the membrane, but, since water components have smaller size, they are able to pass thorough the membrane. Due to this both water flux and rejection increase simultaneously.

Conclusion

The effect of influential parameters on the fundamental characteristics of the membranes such as morphology, wet ability, permeability and rejection were investigated. It was found that the modified PAN membranes with high hydrophilic property can be produced by addition of hydrophilic surfactant, merpol, in the casting solution. Whereas PWF of prepared membranes is increased by adding 2, 4 and 6 wt. % of merpol, further increase in the merpol concentration from 6 to 8 wt. % is decreased PWF. Increase of merpol concentration in the casting solution leads to the increase in insulin rejection of the membranes. It was also found that the less PAN molecular weight leads to the formation of macrovoids along with an increase in pore size. As a result, membranes prepared by PAN 70,000 have higher water permeation and lower protein rejection.

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