Polyethersulfone/polyacrylonitrile blended ultrafiltration membranes: preparation, morphology and filtration properties

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ABSTRACT

Polyethersulfone (PES)/polyacrylonitrile (PAN) membranes have been paid attention among membrane research subjects. However, very few studies are included in the literature. In our study, asymmetric ultrafiltration (UF) membranes were prepared from blends of PES/PAN with phase inversion method using water as coagulation bath. Polyvinylpyrrolidone (PVP) with Mw of 10,000 Da was used as pore former agent. N,N-dimethylformamide was used as solvent. The effects of different percentage of PVP and PES/PAN composition on morphology and water filtration properties were investigated. Membrane performances were examined using pure water and lake water filtration studies. Performances of pure water were less with the addition of PAN into the PES polymer casting solutions. However, long-term water filtration tests showed that PES/PAN blend membranes anti-fouling properties were much higher than the neat PES membranes. The contact angles of PES/PAN membranes were lower than neat PES membranes because of PAN addition in PES polymer casting solutions. Furthermore, it was found that PES/PAN blend UF membranes’ dynamic mechanical analysis properties in terms of Young’s modules were less than neat PES membrane because of decreasing amount of PES polymer.

Key words | flat-sheet membrane, membrane characterization, PAN/PES blend, ultrafiltration

INTRODUCTION

The phase inversion method is one of the most popular methods to fabricate porous polymeric membranes (Meng et al. 1998). In order to get a desired membrane morphology and performance, the phase inversion method must be carefully controlled (Tam et al. 1991; Mulder 1996; Baker 2004). In this method, additives and polymer solution, solvent and non-solvent cast into a film that then converted to a solid state by one of the following methods (Mulder 1996; Baker 2004): (i) immersion precipitation, (ii) precipitation from the vapor phase, (iii) thermal precipitation or TIPS, and (iv) air casting of the dope solution, and (v) precipitation by controlled evaporation.

The thorough study of a synthetic membrane would be incomplete without the appropriate description of its morphology (Tam et al. 1991). One of the most important issues while making a high-performance separation membrane is membrane formation procedure (Koros & Pinnau 1990). For fabrication of high flux and defect-free flat sheet membrane, it is important to bring the dope solution composition around cloud point or the precipitation point by adding proportionate non-solvent additive into the dope (Koros & Pinnau 1990; Pinnau & Koros 1991, 1992). Adding non-solvent additives into the casting or spinning solution can decrease macro-voids formation in the sub-layer (Kesting et al. 1990; Doi & Hamanaka 1991; Kang et al. 1991; Smolders et al. 1992).

Because non-solvent additives decrease the dissolving power of the solvent, polymer–polymer interaction increases. Hence, adding non-solvent into a polymer solution causes the tendency of polymer chains to approach a more tightly coiled conformation (Wang et al. 2002). The precipitation point of the casting solution moves nearer when a non-solvent is added to the polymer solution compared without adding a non-solvent. Non-solvents have the ability to change the phase separation behaviour and can speed up the coagulation process from solution to solid state when immersed in a coagulation bath (Wang et al. 1995; Wang & Teo 1996). On the other hand, polymer
solutions with the addition of non-solvents make the membrane surface thinner and more uniform in structure (Wang et al. 1995). Among them, polyvinylpyrrolidone (PVP) is also known to affect membrane performance favourably (Boom et al. 1992; Chuang et al. 2000; Qin et al. 2003).

Ultrafiltration (UF) is applied for the removal of particles, microorganisms and a certain amount of dissolved organic matter (DOM). UF membrane has been increasingly used in water treatment, separation and purification of different proteins because of its simple and easy-to-use operation process (Ghosh et al. 2000; Muller et al. 2003; Liu et al. 2007; Bhattacharjee et al. 2006; Li et al. 2006; Almeicia et al. 2007; Zhang et al. 2009). Many researchers showed that increasing hydrophilicity of the membrane surfaces and pore walls can remarkably reduce membrane fouling. Because of this reason, various methods such as blending, coating, adsorption, chemical grafting and radiation-induced grafting have been invented (Meincken coating, adsorption, chemical grafting and radiation-induced grafting have been invented (Meincken et al. 2005; Roux et al. 2006; Ulbricht 2006).

It is very difficult to reduce the pore size of polyacrylonitrile (PAN) membrane regarding its poor solubility for various solvents except polar solvents such as N-methyl-2-pyrrolidone (NMP), N,N-dimethylformamide (DMF) and DMAc. The reason why the pore size of the PAN membrane cannot be largely reduced by the phase inversion is poor solubility in mentioned solvents (In-Chul et al. 2002).

Scharnagl et al. (2001) conducted a research about concentration and temperature affects on membrane formation. They found that changing casting solution and temperature lead to different membrane morphologies and pores were vary from finger-like to homogeneous microporous structures. According to (Guo et al. 1996) PAN/PVP blends show single glass transition temperatures over all compositions. Small amounts of additives may control the membrane morphology. One of the most extensively used polymeric additives are PVP and polyethylene glycol (PEG) in the preparation of UF and MF membranes (Madaeni & Pourghorbani 2013). The effect of PVP addition as a pore-forming agent to the casting solution has been widely studied. The higher the molecular weight of PVP entrapped in the membranes during the formation of asymmetric membrane provides the higher hydrophilicity and the resulting membranes turn out to be more hydrophilic. Guo et al. (1996) also mentioned that PAN and PVP blends show conceivable miscibility due to hydrogen-bonding interactions between the $\infty$-hydrogens of PAN and the proton acceptor groups of PVP.

In the present work, development of polyethersulfone (PES)/PAN blend membranes for low fouling tendency in real lake water filtration is proposed and has been tested for the first time in the literature. PES polymer was selected because of high mechanical strength and PAN polymer was selected because of higher hydrophilic properties. PES/PAN membranes were characterized and compared with neat PES membranes in terms of real lake water treatment capabilities.

**EXPERIMENTAL**

**Materials and method**

PES (Ultrason E6020P with the $M_w = 58,000$ Da) was supplied from BASF (Germany). PAN was purchase from Sigma-Aldrich (USA) with the $M_w = 150,000$ Da, $T_g = 85^\circ C$. DMF was supplied as solvent from Merck (Germany). PEG (reagent grade, $M_w = 4,400$, $10,000$ ve $35,000$ Da) supplied by Sigma-Aldrich and PVP 10,000 Da pore former polymeric additive used in the casting solution. PET non-woven substrate (CU434) was supplied from Crane Non-woven (USA) with the porosity of $23.8 \pm 4.6$ cfm.

**Membrane preparation**

A sufficient amount of DMF as solvent was poured up to a glass bottle. Pore forming agent PVP 10,000 Da was added into the DMF solvent. After formation of a homogeneous solution PES and PAN were added to the casting solution. Then PES/PAN solution stirred for overnight at 65°C. The stirring was carried out at 250 rpm. In order to eliminate air bubbles that were entrapped in the polymer solution, an ultrasonic bath (EVEREST Cleanex 401, Turkey) was employed. The viscosity of the prepared casting solutions was measured via AND-Vibrometer (Japan) at a constant temperature of 25°C. The prepared homogeneous solutions were casted on a PET non-woven support layer using an automatic film applicator. The clearance gap between non-woven support layer and film applicator knife was 250 µm. The casted films were submerged into a distilled (DI) water coagulation bath at room temperature (25°C). Membranes, which are cast, were left into the ultra-pure water overnight. The aim of retaining the membranes in the DI water is to remove residual solvents from the membrane matrix. Finally, the membranes were dried using three different concentrations of ethanol/water mixture, respectively (50% w/w, 70% w/w and 100% w/w ethanol/water). Compositions of casting solutions are presented in Table 1.
Membrane characterization

Contact angle measurement

In order to specify the correct contact angle measurement, the membranes were directly measured with a (KSV Atten-sion, Theta, Finland) contact angle measurement instrument. DI water was used as the wetting agent in all measurements. In order to minimize the experimental errors, at least five different measurements were taken from different locations on membrane samples. All measurements were carried out at room temperature (25 °C).

Scanning electron microscopy

Surface characterizations of investigated membranes were examined by scanning electron microscopy (SEM). The samples were dried under dry-air conditions. They were then sputter coated with gold–palladium (Au–Pd) before examination with SEM (FEI, Quanta FEG 250).

Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) test of membranes were carried out in order to see physical effect of PES/PAN polymer blend membranes. The experiments were conducted using a Seiko Japan, SII Nanotechnology DMS6100 (200 Hz) mechanical tester. 10 mm wide and 20 mm long membrane samples were placed into the instrument. The samples were kept immersed in liquid and directly measured when taken from de-ionized water. Membrane samples were taken out from the container and clamped between two aluminum holders. One side of the sample was attached to the holder and the other side attached to a strain-gauge-based force sensor. Each membrane was performed in triplicate with a new membrane sample each time. The mechanical strength of the membranes was completed in two sequential steps. In the first step, stabilization force was applied in the magnitude of 1 N for 5 s to the membrane sample in order to eliminate looseness. In the second step, the upper side of the stage was lifted with a force of 100 mN/min at a maximum value of 10 N.

Permeation experiments

Dead-end UF system

Performances of the prepared membranes were completed using a dead-end UF system. This laboratory scale test system consists of a reservoir, valve, pressure regulator, membrane cell, magnetic stirrer, stone filter, computer and digital balance. All of the materials used in the dead-end UF system were made from stainless steel. Effective area of cell was 14.6 cm². High pressure N₂ gas was used to obtain required pressure for the system. The permeate was collected and weighed in digital balance, then transferred to the computer.

Prior to the UF experiment, prepared membranes were waited in DI water for one week. As a membrane area 14.6 cm² was used in dead-end filtration cell. All membranes were compacted at least 1 h prior to filtration experiment under three bars. Membrane permeability was determined by allowing de-ionized water to pass through the membranes. The filtration cell has a volume of 250 mL. All the experiments were conducted at room temperature (25 °C). Pure water flux (PWF) was calculated as follows in Equation (1):

\[ J_{W1} = \frac{V}{A \Delta t} \]  

where \( J_{W1} \) is the PWF (L/m².h); \( V \) is the volume of permeate (L); \( A \) is the membrane area (m²); and \( \Delta t \) is the permeation time (h). Membrane permeability tests were done at least three times in order to minimize the experimental errors. The same lake water was used for all the filtration experiments. Lake water quality parameters can be seen in Table 2.

RESULTS AND DISCUSSION

In present study, contact angle, SEM, DMA and permeation properties of neat PES and PES/PAN blend membranes were investigated.

<table>
<thead>
<tr>
<th>Number of membrane</th>
<th>(% PES)</th>
<th>(% PAN)</th>
<th>Solvent type</th>
<th>Fabrication temp. (°C)</th>
<th>(% PVP)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>20PES + 2PVP10 (M1)</td>
<td>20</td>
<td>0</td>
<td>DMF</td>
<td>25</td>
<td>2</td>
</tr>
<tr>
<td>20PES + 4PVP10 (M2)</td>
<td>20</td>
<td>0</td>
<td>DMF</td>
<td>25</td>
<td>4</td>
</tr>
<tr>
<td>19.7PES + 0.3PAN + 2PVP10 (M3)</td>
<td>19.7</td>
<td>0.3</td>
<td>DMF</td>
<td>25</td>
<td>2</td>
</tr>
<tr>
<td>19.7PES + 0.3PAN + 4PVP10 (M4)</td>
<td>19.7</td>
<td>0.3</td>
<td>DMF</td>
<td>25</td>
<td>4</td>
</tr>
</tbody>
</table>

*Molecular weight of PVP is 10,000 Da for all membranes.
Hydrophilic properties of a membrane are supposed to be one of the most important parameter in membrane fouling research. One of the most excellent features of PES membranes are good chemical resistance, wide range temperature and desirable mechanical strength. This polymer generally used on membrane properties for various kinds of applications. Hydrophilicity of membranes can be characterized by contact angle measurement (Liu et al. 2005; Roux et al. 2006; Almecija et al. 2007). However, because of the low antifouling property in practical applications, it has some shortcomings (Arahman et al. 2012). In this work, hydrophilic polymer was added to the polymer solution in order to improve the hydrophilicity of PES membrane. Two different amount of PVP (pore forming agent) were blended to PES polymer. The hydrophilicity of blend was observed by DI water contact angle measurements. Membranes were directly measured using a contact angle measuring instrument. Contact angle measurements of membranes directly taken out from DI water, were carried out for both PES/PAN blend and neat PES membranes (Table 3). Salahi et al. (2015) found the same results as our research which is while adding PAN polymer into the PES dope solution surface, contact angle of the membranes tend to show a decreasing trend. As PAN concentration increased, contact angle values tend to decrease, which proves that adding PAN polymer into the PES polymer casting solution has the ability of decreasing contact angle. The results state that blend PES/PAN membranes are more hydrophilic than neat PES membranes.

### Contact angle of prepared membranes

SEMs were performed to find out the qualitative characteristics of the membrane surfaces. In order to understand the effect of membrane modifiers on the membrane structure of neat PES and PES/PAN blend membranes, the characteristics and surface structures of all membranes were investigated via SEM. SEM images of the examined membranes are illustrated in Figures 1 and 2. With the help of SEM images, pore forming agent (PVP) and PAN effect on PES membrane were investigated. The samples were frozen in liquid nitrogen and then fractured. Samples were sputter coated with Au-Pd before examined with SEM.

The effects of PES/PAN composition on the membrane morphology are shown in Figure 3. The membranes prepared from neat PES in Figure 1(a) and 1(b) revealed uniform pore distribution and membranes prepared from M3 and M4 show again uniform pore distribution as given in Figure 1(c) and 1(d). Addition of PAN into PES polymer solution makes the pores smaller. When the casting solution was immersed into the water coagulation bath, the non-solvent and phase separation occurs, demixing at the top layer of the membrane matrix. The SEM surface images indicated that PES/PAN in the casting solution has a significant effect on membrane surface composition.

Because of the nucleation and growth mechanism, affinity between solvent and non-solvent strongly affect the membrane matrix. If the out-diffusion rate of solvent is much higher than the in-diffusion rate of solvent, the top layer is denser, thus lowering the diffusion rate for non-solvent into the sublayer. If the affinity between solvent and non-solvent is weak, a sponge-like structure can be formed (Peng et al. 2010).

The effects of PES/PAN composition on the membrane morphology are shown in Figure 2. The membranes prepared from neat PES polymer in Figure 2(a) and 2(b) revealed macropores. Also, for the second membrane, M2, which is shown in Figure 2(b), the sublayer does not have direct connected pores. The membrane prepared from PES without PAN exhibits a typical asymmetric finger-like structure with sponge structure in its sublayer.

Although increasing the amount of PVP concentration was expected to suppress macropore formation, we could not say it happened as expected. But, membranes prepared from M3 and M4 show better pore formation as given in Figure 2(c) and 2(d). It can be also concluded that a small amount of PAN addition into the PES polymer shows regulatory impact on the final membrane. Both in Figure 2(c) and 2(d), a small amount of PAN into PES polymer paved

### Table 2 | Lake water quality parameters

<table>
<thead>
<tr>
<th>Lake water parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Turbidity</td>
<td>4.25 NTU</td>
</tr>
<tr>
<td>pH</td>
<td>8.4</td>
</tr>
<tr>
<td>Conductivity</td>
<td>330.9 µs/cm</td>
</tr>
<tr>
<td>SS</td>
<td>4 mg/L</td>
</tr>
</tbody>
</table>

### Table 3 | Contact angles of neat PES and PES/PAN membranes

<table>
<thead>
<tr>
<th>Name of the membrane</th>
<th>M1</th>
<th>M2</th>
<th>M3</th>
<th>M4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface contact angle</td>
<td>71.28 ±</td>
<td>71.02 ±</td>
<td>69.20 ±</td>
<td>68 ±</td>
</tr>
<tr>
<td></td>
<td>0.13</td>
<td>0.25</td>
<td>0.25</td>
<td>0.15</td>
</tr>
</tbody>
</table>
the way for pore interconnection. The SEM surface images indicated that PES/PAN in the casting solution has significant effect on membrane cross-section composition.

In order to see PAN deposition in PAN/PES membrane matrix, SEM-EDS Mapping was applied to PAN/PES blend membranes. Yellow dots show PES polymer and green dots show PAN polymer distribution in M3 and M4 blend membranes in Figures 3 and 4. Figures 3(b) and 4(b) show that PAN polymer is uniformly distributed. However, the majority of PAN polymer placed at the top layer of the membrane matrix which is shown with green dots.

Also, when the composition of PAN into the casting solution increases to 0.3%, the interaction between PAN and DMF increases and also a casting solution with lower viscosity is formed (as shown in Table 4). Higher viscosity of the neat PES casting solutions M1 and M2 may collapse the finger-like structure and introduce some macrovoids in the sublayer structure of the membranes (Amirilargani et al. 2012). While adding PVP to PAN/PES polymer blend solution, the viscosity increased relative to the amount of concentration. The higher the polymer viscosity led to the decrease phase separation rates.

Dynamic mechanical properties of neat PES and PES/PAN blend membranes

DMA is one of the most important measurements in membrane physical durability tests. During experiments, while adding PAN into the PES polymer casting solution, the Young’s modulus of PES/PAN blend membranes decreased due to the decreasing percentage of PES polymer in polymer blend. The results are illustrated in Figure 5. Salahi et al. (2015) conducted a research on PES/PAN blend UF hollow fibre membranes for oily wastewater treatment; they found that the tensile strength increases with increasing PAN content in the spinning dope and the addition of PAN to the spinning dope improves mechanical properties of the PES hollow fibre membranes by reducing pore size and brittleness of the membranes. We found similar results with (Salahi et al. 2015), as the small amount of (0.3%) PAN
additions, reducing pore size. But, unlike Salahi et al. (2015) studies (0.3%) PAN additions, PES/PAN blend membrane Young’s modules are lower than PES membranes, and with the increase of PVP addition from 2% to 4% Young’s modules continued decreasing. The reason for that is that while PAN polymer addition to PES dope solution, the PES content in total polymer solution decreases, and it is also known that PAN polymer is more brittle than PES
polymer. So, the increasing amount of PAN led to cause lower Young's modules in PES/PAN blend membranes. PVP 10 kDa agent is another reason for the decreasing of Young's modules of each membrane.

**Permeation properties of the prepared membranes**

Permeation studies carried out for both PES/PAN and neat PES membranes are presented in Table 5. PWF of the blend membranes decreased with increasing amount of PAN polymer in PES/PAN polymer casting solution.

Even in a small amount of PAN (0.3%) addition to the PES polymer blend, permeation properties decrease. The reason for that during phase inversion process is that PAN polymer is collected at the top surface of the membrane. Thus, membrane surface morphology became denser than neat PES membrane surface morphology. PVP, as pore former agent, addition increases the PWF, besides polymer mixture.

**Long-term filtration performance of the membranes**

Long-term filtration studies were carried out under constant pressure by using standard experimental UF setup. Water permeability values are presented in Figure 6. As mentioned
Water filtration studies for all membranes were observed in terms of flux decrease properties.

Appropriate fouling control techniques provide longer membrane life and lower operation costs. Fouling control encapsulates physical and chemical procedures. As physical methods, backwashing, critical flux and transmembrane pressure (TMP) applications, intermittent suction operation, low TMP, high cross-flow velocity and the hydrodynamic shear stress scouring can be applied (Zularisam et al. 2006).

Rejection rates of real lake water contaminants were analysed with total organic carbon (TOC) equipment. Before and after filtration, lake water samples were collected and analysed in terms of its organic content. The results are shown in Table 6. Difference between pre- and post-filtration results were shown that with the addition of PAN to the PES polymer solution membrane rejection rates are increasing.

PAN addition to the PES polymer solution makes M3 and M4 blend membranes’ molecular weight cut-off (MWCO) values smaller.

There was no chemical cleaning applied to the membranes up to first 300 min. Every 60 min, filtration system was stopped and membranes cleaned physically with DI water. As seen in Figure 7, the biggest flux decline was observed in neat PES membrane, M1, because it has the smaller amount of PVP compared with M1 and has higher hydrophobicity. PES/PAN blend membranes have shown less fouling tendency in term of flux decline for the first stage of the experiments. This is related with PAN on PES in terms of layer deposition, which makes the membrane surface more hydrophilic and have shown less fouling propensity. Chemical cleaning was applied after 300 min and percentage of flux decreases were shown in Figure 8.

On the other hand, chemical cleaning agents such as NaOCl, NaOH, HCl and HNO₃ have been shown to recover initial membrane permeability completely (Zularisam et al. 2006). With the help of this information, chemical cleaning was done by NaOH and HCl in order to recover the initial conditions as membrane permeability. For the second stage (after chemical cleaning) lake water filtered by the membranes for another cycle of 300 min. In every 60 min, physical cleaning was made with DI water. As neat PES membranes which are named as M1 and M2, flux decreases were higher than PES/PAN blend membranes.

### Table 5: Permeation properties of neat PES and PES/PAN membranes (at three bars and pH = 7.0)

<table>
<thead>
<tr>
<th>Name of the membrane</th>
<th>M1</th>
<th>M2</th>
<th>M3</th>
<th>M4</th>
</tr>
</thead>
<tbody>
<tr>
<td>PWF (L/m²·h)</td>
<td>132</td>
<td>201</td>
<td>24</td>
<td>66</td>
</tr>
</tbody>
</table>

### Table 6: Real lake rejection rates through membranes

<table>
<thead>
<tr>
<th>Name of the membrane</th>
<th>M1</th>
<th>M2</th>
<th>M3</th>
<th>M4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rejection rates (%)</td>
<td>15</td>
<td>10</td>
<td>26</td>
<td>16</td>
</tr>
</tbody>
</table>
CONCLUSION

In this study, the effects of different PES/PAN composition in the casting solution and different percentage of pore former additives on basic characteristics of both neat PES and PES/PAN blend membranes were investigated. SEM, DMA, surface contact angle, PWF and lake water filtration properties of the membranes were considered. According to the results, the following is concluded:

- Adding a relatively small amount of PAN into the PES polymer solution caused a decrease in PWF properties.
- The surface contact angles of PES/PAN blend membranes were shown to have lower values.
- DMA was shown to have a decreasing trend because of the decreasing percentage of PES polymer in PES/PAN polymer casting solution.
- SEM pictures proved that adding PAN into the PES polymer casting solution made membrane pores smaller.
- Water filtration studies with PES/PAN blend membranes revealed favourable results when compared to neat PES membranes.
- PAN addition to PES polymer solution makes membrane MWCO values smaller compared to neat PES membranes.
- PES/PAN blend membranes were shown to have higher performance in terms of flux decrease before chemical cleaning.
- After chemical cleaning, all membranes' flux show higher values.
At the end of the second 300 min filtration studies, PES/PAN blend membranes completed the tests with lower flux decrease.

- PAN addition into the PES polymer has a pore regulatory effect on the final membrane matrix.
- Membrane fouling is still a phenomenon which cannot be prevented but can be minimized by changing the membrane morphology.

REFERENCES


