Synthesis and characterization of PSF/PES composite membranes for use in oily wastewater treatment

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Abstract
Environmental sustainability requires development of environmentally benign and energy efficient technology for treatment and disposal of wastewater. Membrane technology has emerged as a highly viable method for water treatment throughout the years. However, their limited commercial application has prompted a lot of researchers to explore different approaches to modify the membranes to enhance their performance. Polymer blending is one of the modifying techniques currently being explored to develop materials with unique anticipated properties depending on the type of membrane needed. This technique has shown improvement in the quality of the membrane by enhancing the mechanical strength as well as the performance of the membrane. In this study, blended polysulfone (PSF) and polyethersulfone (PES) membranes were synthesized at different PSF:PES ratios (100%:0%, 0%:100%, 50%:50%, 80%:20%, 20%:80% and 25%:75%) using N-Methyl-2-pyrrolidone (NMP) as a solvent via the phase inversion method. The quality and integrity of the membranes were checked via Scanning electron microscopy (for morphology); Thermogravimetric analysis (for thermal stability), Atomic force microscopy (for surface nature) and nanotensile measurement for mechanical strength. The flux, % rejection and porosity as the performance criteria of membranes showed a massive improvement in majority of the blended membranes than in pure PES and PSF membranes. AFM images indicated lower roughness in the pure PSF membrane as compared to the blended membranes. The tensile strength only improved on the 25%:75% membrane while the elasticity increased with an increase in PES concentration in the blended membranes. These results demonstrate the diversity of blending polymeric membranes to modify specific properties for desired function and highlight the possibility of more commercial application.

Key words: Polysulfone, polyethersulfone, polymer blending, membrane

1. Introduction
Polymeric membranes are continuously being developed to improve their performance and quality, this attracted researchers to the explore different approaches, such as the polymer blending technique both in academic and industrial perspectives [1]. This is because commercial application of polymeric materials as membranes remains technically limited, therefore, there is a serious need for new membrane materials that have different properties from basic polymeric membrane materials [9]. Polymer blending is defined as a physical mixture of two or more polymers which is a time and cost-effective technique used to develop materials with unique anticipated properties depending on the type of membrane needed [12]. However, this technique is limited by the complete incompatibility of certain polymer blends, making it difficult to obtain miscible compositions.
A great majority of polymer blends have been reported to be multiphase, basically partially or completely immiscible. Immiscible polymer blends find it difficult to form a single phase. They have a coarse morphology, sharp interface and poor adhesion between the blend phases [21]. Immiscibility may be limited to certain ranges of temperature, pressure, and composition. It depends on the chemical structures, molar-mass distributions, and molecular architectures of the components [23]. These type of polymer blends are useless without compatibilization. Miscible polymer blends have enthalpy change (ΔH) below 0. The blends often result in a single-phase structure at a particular temperature and are usually optically transparent. Miscibility can be influenced by several factors such as morphology, and reduction of surface tension [21].

Advantages of polymer blending include, increased toughening, extended service temperature range, improved barrier property and flame-retardant property [21]. PES and PSF are reported to be excellent membrane materials widely used for water treatment purposes due to their good membrane forming performances and excellent solubility owing to their good physical and chemical stability [10]. PSF is also reported an excellent polymer for membrane fabrication because it is reported to possess properties needed for efficient water treatment. These properties include good solubility, excellent heat stability, high mechanical strength, electrical and chemical stability [6]. PES on the other hand shows good thermal stability and other properties which include oxidative resistance, visual transparency, and good solubility as well [6], [3]. Thus, it seems very attractive to blend PSF and PES to investigate its effect on the performance, mechanical and thermal stability of the fabricated membranes resulted from the blending.

The rapid growth in the oil, gas and petrochemical industry has led to the large production of oily wastewater made up of different harmful organic compounds [13]. Phenol and benzene are major pollutants largely found in produced water that pose human fatality and threat to the environment. According to the US Environmental Protection Agency, phenol is ranked the 11th most hazardous chemical out of 126 [16]. Benzene is also reported to be volatile and highly soluble in water, which substantially impacts the health human and wildlife exposed to the water [17]. Therefore, there is a need to develop cost-effective technique that will effectively purify water contaminated with these compounds. Therefore, the ultimate aim of this study is to apply the blended membrane to the treatment of this wastewater.

But in this study, the aim was to synthesize blended polysulfone (PSF) and polyethersulfone (PES) composite membrane and select the best one based on its separation performance and quality. Generally, the primary objective of polymer blending was to obtain a membrane with unique improved properties, such as increased flux, mechanical strength and improved thermal stability [21]. Therefore, the goal is to investigate the effect of polymer blending on the flux, mechanical and thermal stability of the membrane. The prepared membranes were characterized in terms of performance, morphology and quality.

2. Methodology

2.1. Materials

The materials employed in the study were polysulfone (PSF) pellets (average molecular weight 35,000 Da) from Sigma Aldrich, South Africa; polyethersulfone (PES) crystal (0.025mm x 150
mm x 150 mm) from GIC Scientific, N-Methyl-2-pyrrolidone (NMP) (99%; from ACE, South Africa), Phenol (Molecular biology) and Benzene (≥ 99.7%) both from Sigma Aldrich, South Africa.

2.2. Membrane synthesis and characterization

A standard procedure was applied when preparing the membranes, using phase inversion technique induced by immersion–precipitation [11]. 10% of Polysulfone and polyethersulfone pellets measured by weight at different compositions of (100:0, 0:100, 50:50, 80:20, 20:80 and 75:25) respectively, were dissolved in NMP under continuous agitation at 60 ºC for 12 h. The casting solution was cast using a casting blade set at ca.180 µm to form the polymeric membrane. The fabricated membrane was then immersed in distilled water for the phase separation step. The formed membranes were left to dry at room temperature for 24 hours. The membranes were then characterized.

Equilibrium water content (EWC) and porosity

EWC is directly related to porosity and is defined as the moisture level where the membrane neither loses nor gains moisture [8]. It was calculated using equation (1), where $W_w$ is the weight of the membrane when wet while $W_d$ is the dry weight of the membrane.

$$EWC = \frac{W_w - W_d}{W_w} \times 100\%$$  \hspace{1cm} (1)

Porosity of the membrane was determined by the mass loss of wet membrane after drying up [8]. It also measures up the void spaces created by pores within the membrane. It was calculated using equation 1, where $\rho$ is the density of water and $V$ is the total volume of the membrane [20].

Atomic Force Microscopy (AFM)

AFM was used to record topographic images of the membranes and provide some information on the roughness of the samples. The information is gathered with sharp tip that is connected to the end of the cantilever. This tip scans the surface of membrane, and forces between the tip and the membrane surface “lead to a deflection of the cantilever according to Hooke’s Law” [20]. The AFM was operated in non-contact mode, at a resonance frequency between 75-100 kHz and 1µm×1µm images were obtained.

Thermogravimetry analysis (TGA)

The membranes degradation ability was investigated using a thermogravimetry analysis (TGA) instrument. Measurements were carried out under nitrogen atmosphere, in the temperature range from 25 to 800 ºC, at a flow rate of 50 ºC. The thermal stability of both PSF and PES membranes were measured to serve as reference point for the blended membranes.

Nano-tensile tester
A tensile test was conducted on the membrane using a nano-tensile test machine. Three samples of each membrane with a dimension of 10 x 30 mm$^2$ were cut and tested. The force applied at break and difference between the length prior and length after breaking for each sample were obtained. Finally, the tensile strength and young modulus values were analyzed using Equation 2 and 3 respectively.

\[
\text{Tensile Strength} = \frac{\text{Force}}{\text{Area}} \quad (2)
\]

\[
\text{Young Modulus} = \frac{\text{Tensile Strength}}{\text{Strain}} \quad (3)
\]

2.3. Pure water permeation

Pure water permeation is well-defined as the volume of permeate that passes through a membrane per unit membrane surface per unit time and it is related to water permeation which is a pressure driven process [19]. The flux of the synthesized composite membranes was measured using a dead-end filtration unit. The flux was obtained using equation 4 where $J_w$ represents pure water flux (L/m$^2$h), $V$ is the volume of water (L) that permeated through the membrane, $A$ represents the membrane area (m$^2$) while $t$ stands for water permeation time (h).

\[
J_w = \frac{V}{A \Delta t} \quad (4)
\]

2.4. Phenol and benzene wastewater separation

The ultrafiltration experiment was conducted using a dead-end filtration unit to evaluate the separation performance of PSF/PES blending for phenol and benzene wastewater. To prepare the feed, phenol and benzene were dissolved in deionized water at a concentration of 30 mg/L and 50 mg/L, respectively. The feed was filtered through each membrane and the permeate was analysed using a pre-calibrated GC-MS. Rejection ratio was calculated using equation 6, where $C_p$ is the concentration of the permeate while $C_f$ is the concentration of the feed. For each membrane, three permeation tests were conducted, and the average rejection values are reported.

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R (\%) = (1 - \frac{C_p}{C_f}) \times 100 \quad (5)
\]

3. Result and discussions

3.1. Membrane synthesis and characterization

Six membranes, PSF, PES and 4 blended PSF/PES were prepared using the phase inversion method. NMP was the solvent of choice because it is a polar solvent, its ability to evaporate at room temperature facilitates the formation of pores on the membrane surface [2]. The prepared membranes were characterized and evaluated for their performance.

3.1.1. Membrane characterization by EWC and porosity
The equilibrium water content of the prepared membranes was measured as shown on Table 1 using equation 1. This is an important parameter for membrane characterization, it has a close association with pure water flux because flux relies on the number of pores on the surface of the membrane. These pores allow the membrane to accommodate water molecules. The results on the table below show that the water content of pure PES membrane is greater than that of pure PSF, and when the two polymers are blended, the water content only shows an improvement when both the polymer weight are the same and when it is slightly different. This is evident with the 50%PSF-50%PES which has the highest water content followed by the 25%PSF-75%PES membrane.

Porosity of the membranes was determined by analysis of its weight in the wet and dry state, it was calculated from Equation 2 and the results are presented on Table 1. As observed, the porosity of PES, 43.15% is greater than that of PSF, which is 38.66%. Blending PSF with PES enhances its porosity when the wt% of PES is greater or equal to PSF, 50%PSF-50%PES membrane showed the highest porosity of 55.39%.

Table 1: Effect of polymer blending on ultrafiltration characteristic of membranes

| Membrane       | EWC    | Porosity    |
|----------------|--------|-------------|
| 100% PSF       | 55.83% | 38.66% ±6   |
| 100% PES       | 61.94% | 43.15% ±4.8 |
| 20%PSF – 80%PES| 54.95% | 48.66% ±3   |
| 25%PSF – 75%PES| 61.58% | 55.39% ±5.6 |
| 50%PSF – 50%PES| 72.52% | 58.87% ±3.7 |
| 80%PSF – 20%PES| 53.10% | 37.70% ±2   |

3.1.2. Thermal stability

The membranes degradation potential was studied using a thermogravimetry analysis (TGA) instrument. The Thermo-Gravimetric Analyses of PSF, PES and PSF/PES blend membranes are shown in Fig 1. As observed on Fig.1, the thermal stability of both PSF and PES membranes was measured as reference to the blended membranes, the PES curve shows to be the least stable, it begins to lose mass just above 400 °C, as compared to the PSF membrane curve which begins to lose its mass around 500 °C. The PES graph is slightly comparable to that observed in [3] which also decomposed before reaching 600°C. It is also shown that blending PES with PSF enhances its thermal stability. Very little weight loss is observed under 500 °C for all blended membranes, indicating good heat resistance. Amongst all, 25%PSF-75%PES membrane shows to be the most stable. Fig.2 shows the derivative weight loss curve and the entire have a single peak, which confirms miscibility of both polymers, proving that no phase separation took place during blending.