

# Chromium (III) Removal by Epoxy-Cross-Linked Polyethersulfone Ultrafiltration Membrane

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## Article history

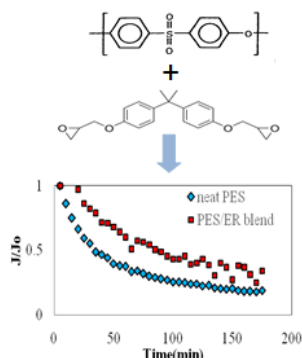
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## Graphical abstract



## Abstract

This study attempts to correlate the changes in membrane morphology with the separation efficiency of the polyethersulfone/epoxy resin (PES/ER) blend membranes. Intermolecular interactions between the components in PES/ER blend membranes were established by ATR-FTIR and the morphological study by field emission scanning electron microscopy (FESEM) has confirmed the significant changes of pores connectivity between the sub-layers of membrane. PES/ER blend membrane with 10% of ER revealed highest rejection of Cr(III) ions at 85% without jeopardizing the permeate flux (12.17 L/m<sup>2</sup>h). From the results, it could be concluded that the PES/ER blend membrane has the great potential in the removal of chromium ions from an aqueous waste.

**Keywords:** Epoxy resin; polyethersulfone; membrane; chromium removal; ultrafiltration

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## 1.0 INTRODUCTION

Various industrial processes such as electroplating, leather tanning and metal finishing requires a big consumption of chromium [1, 2]. The waste water from these industries usually contained of higher level of chromium ions. The removal of heavy metal from inorganic effluent can be achieved by conventional treatment processes such as chemical precipitation, ion exchange, and electrochemical removal. However, these processes suffered significant disadvantages, which are for incomplete removal and high-energy requirements [2].

Over the past few decades, major advances have occurred in both understanding and practice of membrane technologies in recovery of chromium from residual waters. The membrane technologies has represents an economic advantage, especially for their high efficiency, easy operation and space saving [3, 4]. Polysulfone (PS) and poly(ether)sulfone (PES) are those of the attractive materials for membrane separation because of their good mechanical and high thermal and chemical stability. However, application of these membranes are restricted because of its drawbacks such as the high hydrophobic nature which leads to severe fouling during macro molecular separations [5].

Thus, it is desirable to make the membrane more hydrophilic to enhance its fouling resistance and separation efficiency.

The separation performance of a membrane can be improved by blending it with an appropriate polymers, in view of the fact that the polymer blends have provided an efficient way to fulfill new requirements for material property [6, 7]. The high porosity, hydrophilic, good resilience character and abrasion resistance of epoxy resins (ERs) make them possible to be incorporated into the polymer matrix to introduce hydrophilicity in the resultant blend membrane. Hence, achieve optimum membrane performance in terms of flux, water content and membrane resistance [8]. Recently, cellulose acetate-epoxy resin blended ultrafiltration membranes have been prepared and applied for the rejection of proteins and heavy metal, where both separation performances have achieving more than 90% of rejection [9, 10]. As for the research carried out by Mahendran and co-workers [9], Bisphenol A diglycidyl ether (DGEBA) was blended with cellulose acetate in order to increase the hydrophilicity of the CA/DGEBA blend membrane, which proved has achieved in better solute rejection and flux [9].

In this research, we intend to increase the filtration performances of PES membrane by introducing epoxy resin

material into the polymer matrix. However, the main challenges to integrate epoxy group to the polymer is about the ratio of the epoxy resin that added into the polymer solution. In this study, the effect of polymer/epoxy resin blend composition on the morphology, rejection and permeate flux of Cr(III) were investigated. Correlation between the morphologies of the PES/ER blend membranes with permeation flux and rejection of the chromium ions are discussed.

## 2.0 EXPERIMENTAL

### 2.1 Materials

Polyethersulfone (PES, Ultrason E6020P, MW 58,000 Da) was supplied by BASF. 1-Methyl 2-pyrrolidone (NMP) used as solvent to dissolve PES polymer and Bisphenol A diglycidyl ether (DGEBA) epoxy resin (ER) were purchased from Merck (Germany) and Aldrich (Switzerland), respectively. The feed Cr solution was prepared using potassium chromate supplied by Aldrich (Switzerland). Reagents used to detect Cr concentration (Acid Reagent Powder Pillows, ChromaVer® 3 Chromium Reagent Powder Pillows, Chromium Reagent Powder Pillows) were purchased from Arachem (M) Sdn. Bhd.

### 2.2 Membrane Preparation

A series of PES membranes were synthesized, as their composition is tabulated in Table 1. Casting dope was prepared by dissolving the PES polymer in NMP solvent and stirred for 5 h at 25°C. Epoxy resin (ER) was then added to the PES/NMP mixture and the stirring process was continuing for 3 h until a homogenous solution was obtained. Prior to membrane casting, the dope solution was degassed for 3 h to eliminate the air bubbles. A film applicator was used for membrane casting. Dope solution was casted on a glass plate using a stainless steel casting blade adjusted to 250 µm clearance gap. The casted film was then allowed for dry phase inversion in a glove box under humidity level of 50-55% for 20 min, and then immersed into the coagulation bath (distilled water) for 24 h.

**Table 1** Composition of PES/ER membrane prepared

Membrane	Polymer Composition (15 wt.%)		Solvent
	PES (wt.%)	ER (wt.%)	NMP (wt.%)
Neat PES	15	0	85
10% EPES	13.5	1.5	85
20% EPES	12	3	85
30% EPES	10.5	4.5	85

### 2.3 Characterization

ATR-FTIR spectra of pure ER and synthesised membranes were analyzed using Thermo Scientific Fourier transform infrared spectrometer (NICOLET iS10, USA). Each spectrum was obtained from 32 scans at a 45° incident angle using a diamond crystal over the wavenumber range of 4000-600 cm<sup>-1</sup>. The surface and cross-sectional morphology of the membranes were visualized using Field Emission Scanning Electron Microscopy (SUPRA TM 35vp Zeiss) at an accelerating voltage of 5 kV. For cross-sectional analysis, the membranes was fractured using

liquid nitrogen. All membrane samples were first coated with platinum (Pt) to prevent a charge on the surface.

### 2.4 Membrane Performance

Ultrafiltration was carried out in a batch type, dead-end cell (Sterlitech, HP4750 Stirred Cell) with internal diameter 49 mm with an effective membrane area of 18.86 cm<sup>2</sup>. 1 mg L<sup>-1</sup> of Cr solution was used as the feed solution and the nitrogen gas was used to pressurize the filtration test rig at 7 bar. During filtration, the feed solution was stirred at the stirring speed of 250 rpm by using a magnetic hotplate stirrer. The accumulated permeate mass which will be used to calculate the filtration flux (J, L/m<sup>2</sup>.h) was read by a computer-recorded electronic balance (FX3000i AND, USA) at an interval time of 5min. The concentrations of Cr obtained from the accumulated permeate were then measured using DR 5000 Hach Spectrophotometer (USA).

## 3.0 RESULTS AND DISCUSSION

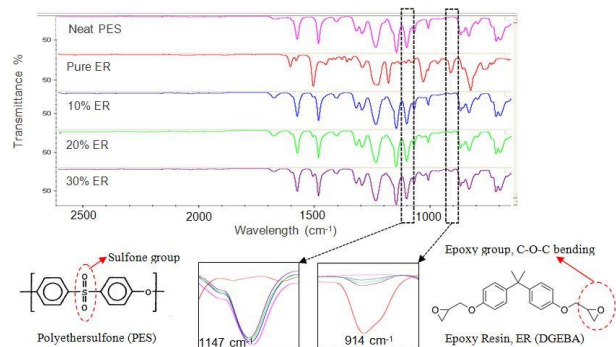
ATR-FTIR was used to characterize the synthesized PES/ER membranes, as the spectra are shown in Figure 1 and the peak assignments are given in Table 2. As can be seen in Figure 1, both neat PES and PES/ER membranes (10% ER, 20% ER and 30% ER) demonstrated the sharp peak at 1147.85 cm<sup>-1</sup>, indicated the symmetric vibration of the S=O stretching sulfone group of PES membrane [11]. As expected, this peak was not existed as for the pure ER. The spectrum of pure ER has demonstrated a sharp peak at 914 cm<sup>-1</sup>, due to the stretching frequency of C-O-C bending of epoxy group (characteristic oxiran ring vibration) existed in the resin [12, 13]. This peak, do not appear at the neat PES membrane but revealed in 10% ER, 20% ER, and 30% ER of PES/ER blend membranes, respectively. The existed C-O-C stretching groups in the blend membranes proves the successful integration of epoxy resin within the PES polymer. The hydrophilic nature of the epoxy resin, is expected to reduce the fouling behavior of the resultant membranes with higher permeation flux. With the good resilience character of epoxy resin, the PES/ER blending is also anticipated to further enhance the chemical stability of the resultant membrane for higher rejection of Cr<sup>3+</sup> ions.

**Table 2** FTIR peaks in the pure ER and PES/ER blend membranes

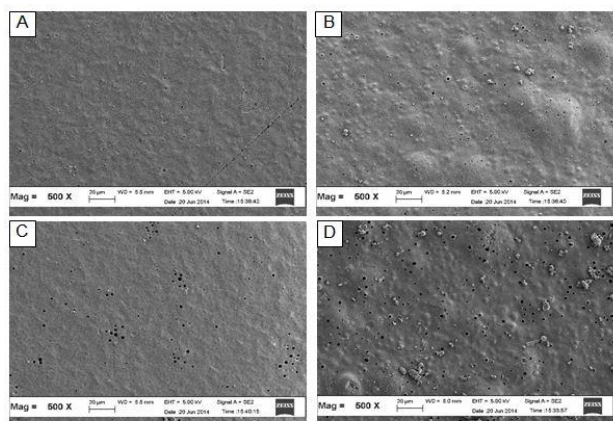
Group	Wavelength(cm <sup>-1</sup> )				
	Neat PES	ER	10% EPES	20% EPES	30% EPES
Sulfone, S=O stretch	1147.85	-	1148.52	1148.91	1149.34
Epoxy, C-O-C bend	-	914.1	914.5	914.9	914.77

Figure 2 represents the surface morphologies of neat PES and a series of PES/ER blend membranes prepared at different concentration of epoxy resin. As shown in the FESEM micrographs, the smooth surface of the neat PES membrane (Figure 2A) was altered to a relatively rough surface when ER was blended with the PES polymer (Figure 2A-D). In fact, PES/ER blend membrane with 30% ER (Figure 2D) has demonstrated the biggest surface pores followed by 20% ER and 10% ER membrane. The increased of surface pores could be explained through the kinetic point of view where the dope viscosity will be emphasized. As for the manufacturing of the

DGEBA epoxy resin, the low viscosity of glycidyl ethers has been added to reduce the overall viscosity of Bisphenol A for better handling purposes. Hence, the incorporation of epoxy resin in the casting solution would produce a lower viscosity mixture. Since the total polymer compositions (consisted of PES and ER) was fixed at 15 wt.%, the viscosity of the dope solution will be decreased as more ER was added into the casting dope. The lower dope viscosity will then reduce the polymer precipitation at the membrane-air interface, which hastened the inter-diffusion rate between the solvent (NMP) and non-solvent (water vapor from the humid surrounding). Thus, leading to a faster phase inversion and bigger surface pores were created.



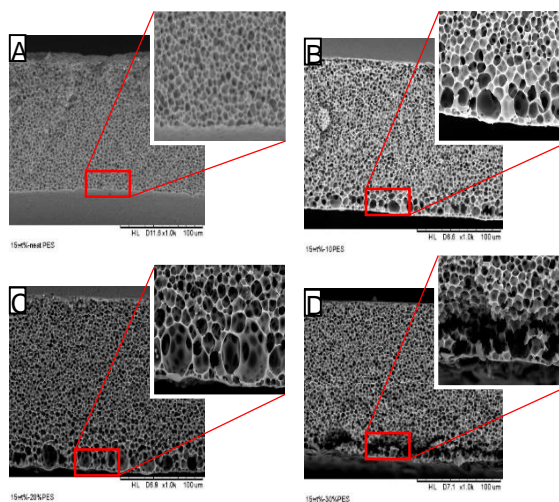
**Figure 1** FTIR spectra of Neat PES, 10% ER, 20% ER, 30% ER membranes and pure ER



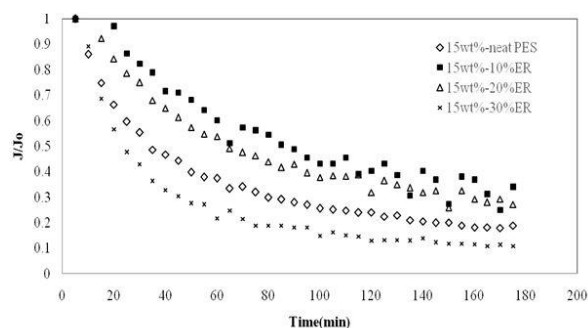
**Figure 2** FESEM micrograph for top surface of (A) neat PES (B) 10% ER (C) 20% ER and (D) 30% ER membranes

Furthermore, the presence of macrovoids could be observed from the cross section of membranes formed with 30% ER (Figure 3D). The formation of macrovoids became more significant when higher amount of ER was added to the casting dope. In contrast, the neat PES membrane was appeared as a homogenous porous film for the entire scanned area of cross-section. The appearance of macrovoids in the membrane internal layer could be related to the membrane formation mechanism [14]. When more epoxy resin was added, it produced lower viscosity of casting dope. As for phase inversion process, the formation of nuclei is started at the region near to the membrane surface area, where the lower viscosity of casting dope will eventually caused faster phase separation. Finally, the macrovoids are formed due to the fast outward diffusion of solvent and displacement of the non-solvent in the casting film. In this work, we observed the formation of bigger voids near to

the membrane-glass interface when higher amount of epoxy resin was added.



**Figure 3** FESEM micrograph for cross-sectional of (A) neat PES (B) 10% ER (C) 20% ER and (D) 30% ER membranes



**Figure 4** Normalized flux for the filtration of 1 mg L<sup>-1</sup> solutions of Cr(III) on neat PES and PES/ER membranes

The filtration performance of the neat PES and PES/ER blend membranes are shown in Figure 4 and Table 3. The neat PES membrane has demonstrated high initial flux at 37 L/m<sup>2</sup>h. Unfortunately, the membrane fouled rapidly within 3 hours of filtration to normalized flux of 0.17. In contrast, the PES/ER blend membranes (10% ER and 20% ER) showed a better antifouling capacity compared to the neat PES membrane. The observed better antifouling properties for the PES/ER blend membrane was attributed to the hydrophilic nature of epoxy resin, making the membrane more hydrophilic and susceptible to fouling. Whilst, an over-dosage of epoxy resin (referred to 30% ER in current work) has caused bigger surface pores (Figure 2) and formation of macrovoids (Figure 3). As expected, the highest initial flux was observed at 42 L/m<sup>2</sup>h (membrane with 30% ER). Unfortunately, the membrane was also demonstrated a serious fouled as similar to the neat PES membrane.

Although PES membrane has showed a considerable high initial flux in this work, however, it has performed the lowest rejection rate of Cr(III) at only 14%. This is due to the hydrophobic nature of the membrane which will further caused the higher attachment of Cr(III) ions near to the membrane surface and reduced the rejection rate. As evidenced in Figure 4, although the initial flux of neat PES membrane was high, but it

fouled more rapidly compared to the 10% ER/PES and 20% ER/PES membranes after the same testing period of 3 h. With the presence of epoxy resin in the membrane matrix, the blend membranes has demonstrated better rejection rate of Cr(III) ions. In fact, the 10% ER membrane give the highest Cr(III) ions rejection at 85%, which is 6 times higher than the neat PES membrane (Table 3). Thus, it proved the practicability of epoxy resin in improving the membrane hydrophilicity that further showed greater resistance to fouling with better rejection rate. This result is in accordance with the findings by Jayalakshmi and co-workers [10]. According to Jayalakshmi *et al.* [10], the introducing of epoxy groups into the PES backbone could improve the hydrophilicity and selectivity of the PES membranes, where the epoxy functionalized PES can be used as the hydrophilic modification agent for the development of high performance ultrafiltration membrane. However, when more epoxy resin was introduced into the casting dope (20% ER and 30% ER), the rejection rate of Cr(III) ions was shown decreasing. This is simply due to the bigger surface pores and the formation of macrovoids, as discussed earlier.

**Table 3** Initial Flux and percentage rejection of the Cr(III) ions by PES/ER blend membranes

Membrane	Initial Flux, $J_0$ (L/m <sup>2</sup> h)	Percent Rejection of Cr(III) ions (%)
Neat PES	32.71	14.29
10% ER	12.17	84.76
20% ER	26.76	47.62
30% ER	41.98	33.33

#### 4.0 CONCLUSION

The effects of epoxy group on the PES membrane were studied by evaluating the surface morphology, flux, fouling resistance and the efficiency on removal of Cr(III) ions. FTIR analysis revealed the presence of epoxy group, C-O-C bending on the PES membrane when ER was added at different composition. Morphology studies show the adding of ER into the PES solution increase the membrane porosity which later increase the overall permeation flux of the membrane during filtration. PES/ER blend membrane with 10% of ER revealed highest rejection of Cr(III) ions at 85% without jeopardizing the permeate flux (12.17 L/m<sup>2</sup>h). The overall PES/ER blend membrane demonstrated consecutively reduce propensity of fouling and maintain at high rejection of Cr(III) with good resilience character of resin.

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