

# Morphological analysis of Polyethersulfone/polyvinyl Acetate blend membrane synthesized at various polymer concentrations

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**Abstract.** This paper reports the effect of varying polymer concentration i.e. solvent/polymer ratio on the morphology and gas transport behaviour of polyethersulfone/polyvinyl acetate blend membrane. The solvent used was dimethylformamide, while the manipulated variable was polymer concentration. The concentrations were varied from 75-90 weight % solvent. A homogeneous surface with dense cross-section structure membranes were successfully developed as deduced from FESEM images. The permeability of CO<sub>2</sub> and CH<sub>4</sub> gases increased with increasing polymer concentration and an improved CO<sub>2</sub>/CH<sub>4</sub> selectivity was observed. These observation made from the characterization justified the applicability of the blend to be synthesized as membrane for gas separation.

## 1. Introduction

The current specification of carbon dioxide (CO<sub>2</sub>) content in natural gas composition as per US pipeline grid is less than 2%, which urges the advancement of natural gas treatment technology [1]. As compared to other conventional method, membranes are becoming a reliable alternative method equipped with attractive features such as its simple operation, low energy and maintenance requirement, environmental friendly as well as high separation performance [2]. Developments of membrane material usually consist of polymeric and inorganic membrane, where native polymeric membranes have been recognized as a competent membrane base material since 1980s. However, the empirical trade-off between the intra-segmental mobility and inter-segmental packing as demonstrated by Robeson through the upper bound plot in 1991 and 2008 [3] where their performance are still below the par, becomes the challenge to be implemented in industrial scale. The separation performance of a membrane is justified by calculating the permeability and selectivity of the membrane towards the test gases (i.e. CO<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub>). However, this performance key feature is directly proportional to its morphology and physico-chemical properties, thus modification needs to be done to improve the performance of pristine polymer [4].

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Various enhancement methods have been carried out to improve the performance of pure polymeric material as a membrane base material, such as incorporation of polar groups (i.e. amines), coating with poly(dimethyl siloxane), crosslinking, production of fixed carrier membranes, increasing the free volume by incorporation of nanoparticles and polymer blending [5]. Above all, polymer blending is an attractive alternative in terms of economical and energy-efficiency point view whilst not only retaining the attributes from desired individual polymer, yet producing a new material with synergistic properties.

The existence of polar acetate group in PVAc polymer chain structure increases its competency as a potential membrane base material, together with easy film forming attributes [6]. However, fabrication limitation is the major issue in its individual applicability that urges the enhancement of its mechanical properties. Thus, blending of PVAc with a polymer of high chemical resistance as well as good mechanical properties, more likely from glassy polymer group is preferable. In addition to PES good mechanical properties and chemical resistance, its ether-oxygen which provides a binding mode for CO<sub>2</sub>, became the prominence benefit [7]. The combination of these two materials will provide three binding modes for CO<sub>2</sub> which is preferable in solution-diffusion gas separation mechanism and more likely being able to separate CO<sub>2</sub> from other gases [6].

Herein, we investigated the effect of polymer concentration on the polymeric blend membrane, taking PES and PVAc as the component polymers. The developed membranes were prepared by solvent evaporation method. The morphology, inter-polymer interaction, and miscibility of the developed membranes were studied by FESEM, FTIR, and DSC respectively.

## 2. Experimental

### 2.1. Materials

Polyethersulfone (PES ULTRASON® E-6020 P) with MW of 50,000 g/mol was purchased from BASF. The PES flakes were pre-treated prior to processing at 105°C for 24 hours to remove moisture. Polyvinyl acetate (PVAc) beads with MW of 100,000 g/mol supplied by Sigma Aldrich were used as received. The solvent used to prepare the dope solution was Dimethyl formamide (DMF) EMPLURA®, supplied from Merck, Germany.

### 2.2. Membrane preparation

The method of solution casting and solvent evaporation were used to prepare the membrane. The blends were prepared according to optimum (90/10) polymer ratio with manipulation of the solvent/polymer ratio [8]. The blend with composition of 75-90 wt. % solvent/polymer ratios were labelled as Blend 1, Blend 2, Blend 3, and Blend 4, respectively. As a comparison, pure glassy and rubbery membranes were developed as well as shown in Table 1.

**Table 1.** The composition and thickness of the developed membrane

Membrane	Composition (wt %)	Thickness (μm)	Glass Transition Temperature (°C)
Pure PES	19.6	216.0	210.0
Pure PVAc	19.6	243.8	31.95
Blend 1	10.0	88.0	182.5
Blend 2	15.0	67.7	182.5
Blend 3	20.0	97.4	188.5
Blend 4	25.0	46.0	186.3

The dope solutions were prepared by dissolving the component polymers in a closely-tight blue cap bottle using DMF as solvent for 24 hours. The dope solutions were degassed for an hour to remove the bubbles formed during mixing process. For homogenization process, the dope solutions were left to stand at room temperature for 2 hours. The pure PVAc polymer was casted on a Teflon plate due to its sticky nature, while others were casted on a glass plate using an adjustable knife casting machine at 100  $\mu\text{m}$ . The casted flat sheet membranes with half A4 size were dried at room atmosphere for three hours in an aluminium foil-closed tray prior to drying in vacuum oven at 90°C for 24 hours. Finally, the developed membranes were left at room temperature to dry completely. The thickness of the developed membranes was measured using FESEM analysis and summarized in Table 1.

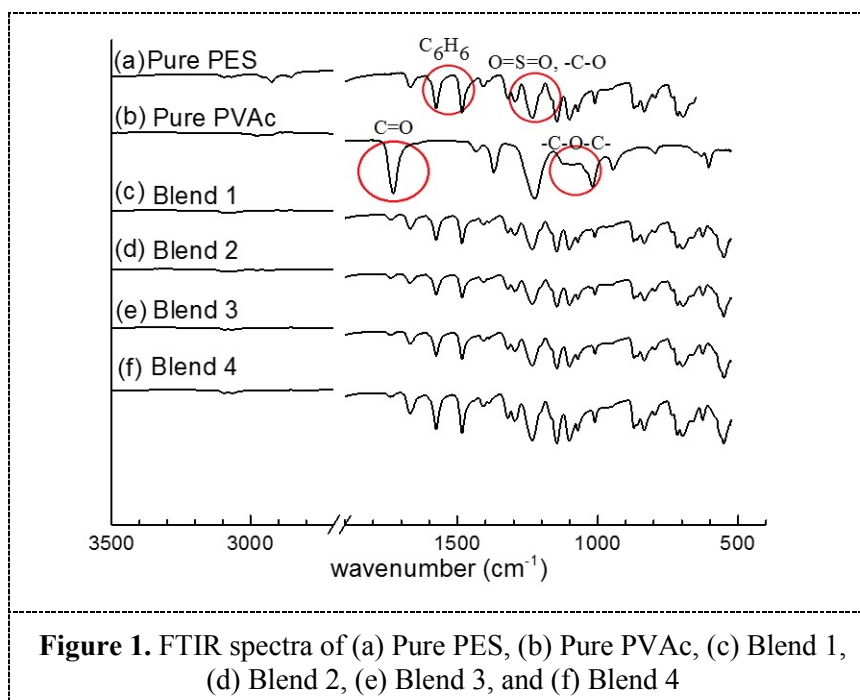
### 2.3. Membrane Characterization and Gas Permeation Studies

Fourier transform infrared (FTIR) spectroscopy study was used to determine the functional groups exhibited in the developed blend membranes. The infrared was collected under Nicolet iS10 FTIR Spectrometer in the frequency range of 500–4000  $\text{cm}^{-1}$ . The morphology of the membranes was observed under field emission scanning electron microscope FESEM (ZEISS SUPRATM 55VP). The membranes were fractured in liquid Nitrogen prior to imaging step. In order to justify the miscibility of the developed blend membrane, differential scanning calorimetry analysis (DSC) analysis had been carried out. The glass transition temperature  $T_g$  of pure and polymer blend membranes were observed by Mettler Toledo model DSC-1 equipment. The detailed aspect of gas permeability unit and procedure for gas permeability analysis were described in our previous work [9]. The gas permeation experiments were performed at 25°C and 4 bar pressure.

## 3. Results and Discussion

### 3.1. Fourier Transform Infrared Spectroscopy

The effect of polymer concentration at fixed blend ratio towards the stabilization of inter polymer bonding, foremost the hydrogen bonding was analysed under the FTIR spectrum as presented in Figure 1.



**Figure 1.** FTIR spectra of (a) Pure PES, (b) Pure PVAc, (c) Blend 1, (d) Blend 2, (e) Blend 3, and (f) Blend 4

The FTIR spectra of PES/PVAc blend membranes (Figure 1.c-f) have similar trends as their component polymers. However, the characteristic peaks are shifted. The effect of blending on the inter

polymer interaction has been studied previously, which shown that the component polymers interact at the molecular level, apparently justified by the shift of the wavenumber of the potential functional group to the lower scale, where the potential functional groups in each polymer are the one who tends to interact via hydrogen bonding [10]. The sulfone groups ( $\text{O}=\text{S}=\text{O}$ ) has the most significant shift from the pure PES polymer, where they move from  $1297.43\text{ cm}^{-1}$  to lower wavenumber around  $1296\text{ cm}^{-1}$  (the discrepancy of the wave numbers depended on the polymer solution concentration). A shift of the ether oxygen of pure PES was shifted from  $1273.79\text{ cm}^{-1}$  to around  $1232\text{ cm}^{-1}$ . Besides, the broad band of carbonyl group of pure PVAc shifted from  $1728.00\text{ cm}^{-1}$  to around  $1667\text{ cm}^{-1}$ , while the ester oxygen of this compound shifted from  $1019.24\text{ cm}^{-1}$  to around  $1010\text{ cm}^{-1}$ . These movements of the component polymers functional groups portrayed the existence of hydrogen bonding in the system [2]. The shifting of the aromatic benzene group is not significant as the group is already stable which is impossible to create hydrogen bonding.

### 3.2. Morphology of Blend Membranes

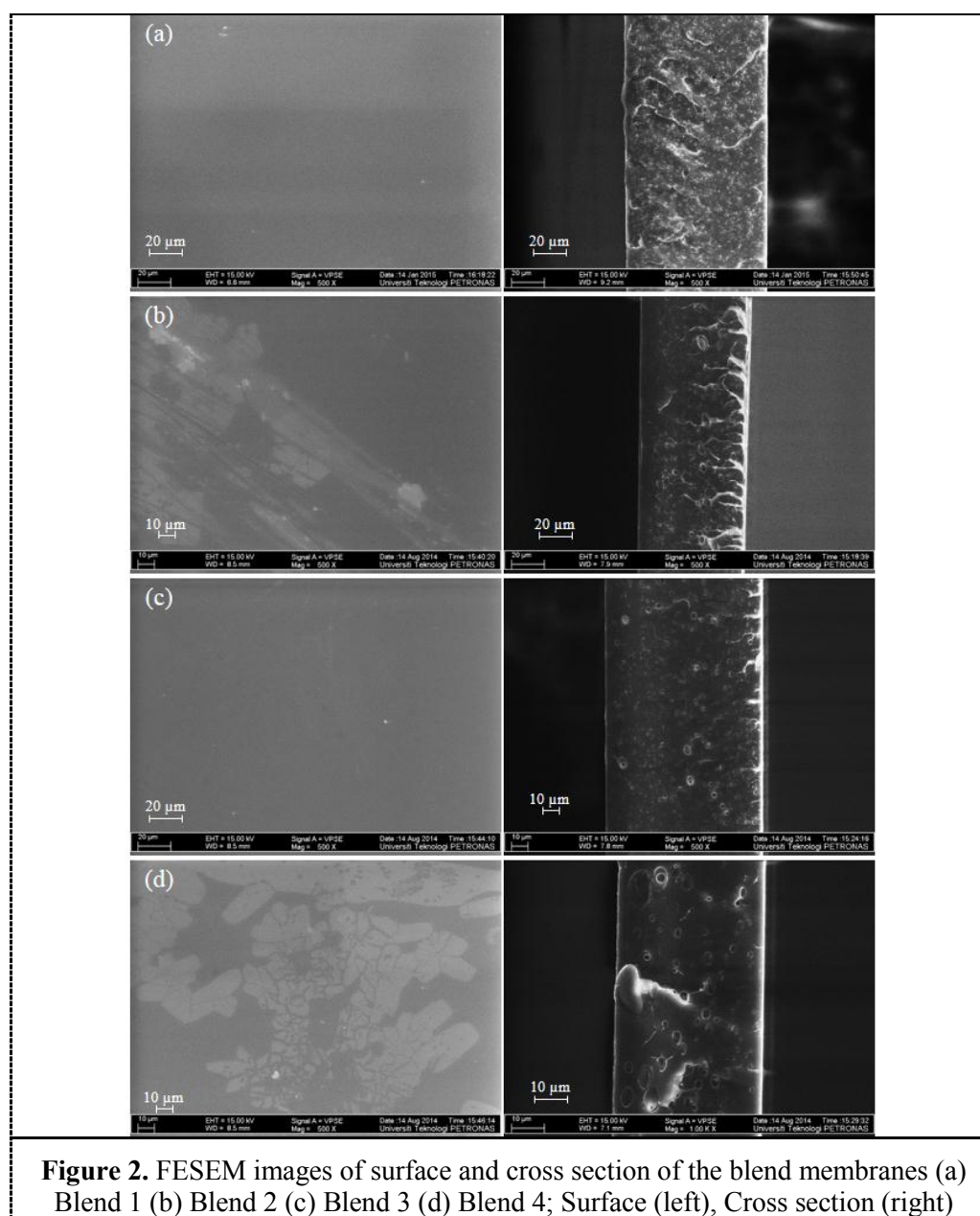
The morphological study of the cross section of the developed membranes was imaged under FESEM analysis, as shown in Figure 2. The microstructure images exhibit homogeneity of the polymers pair with dense structure, however, the cross-sectional views of the developed membranes showed the presence of micro pores. However, the blend membrane apparently showed no phase separation. Besides, it was observed that the number of pores reduces with increasing solvent/polymer ratio. This observation is in line with the reported studies on the effect of polymer concentration in hindering the micro pores formation. However, Blend 4 shown a big pore defect which correspond from the membrane-glass plate detachment effect which affecting its thin membrane thickness ( $46.0\text{ }\mu\text{m}$ ). Bakeri et al. [11] and Rafiq et al. [12] observed similar suppression effect of the micro pores formation as they studied the effect of critical polymer concentration in the development of membrane for gas separation. The FESEM images of the pure component polymers can be found in the previous work [8]. These dense structures without any defect i.e. pinholes or cracks observed from the cross-section views of the developed blend membranes with respect to the pure component polymers suggest the miscibility is attained between the component polymers [2]. Both polymers are well dispersed in each other, where at varied polymer concentration, no phase separation is observed.

### 3.3. Differential Scanning Calorimetry (DSC) Analysis

The miscibility of the polymers upon blending can be justified with DSC analysis with the existence of single glass transition temperature in the blend for the pairs with significant difference in  $T_g$  [13]. Table 1 summarizes the  $T_g$ 's of the developed membranes. It is observed that each blend displayed a single glass transition temperature, intermediate between the pure polymeric membranes and slightly varies with varying solvent/polymer ratios. This suggests the miscibility is attained by the blend. From the table, the  $T_g$ 's of the developed blend membrane varied with different polymer concentration, however, the difference is not really significant. The lower the polymer concentration, the more reduction from the  $T_g$  of the pure PES membrane.

### 3.4. Gas Permeability Studies

Table 2 shows the preliminary investigation of gas permeation properties of synthesized membranes at  $25^\circ\text{C}$  and 4 bar pressure. The performance of blend membranes can be compared with pure PES and PVAc membrane [8]. By increasing the polymer ratio in the dope solution, the  $\text{CO}_2$  permeability is reduced from 19.97 barrer to 0.42 barrer and then shows a gradual increase and reaches to 1.00 barrer and finally the permeability of Blend-4 membrane is recorded as 11.59 barrer. A similar behaviour is observed for  $\text{CH}_4$  permeability and ideal selectivity. This is due to the fact that by increasing the polymer ratio in dope solution the cross section of membrane represents a defect free dense structure which caused a decrease in permeability and an increase in ideal selectivity.

**Table 2.** Gas permeation performance of blend membranes at 25°C and 4 bar pressure

Sample	CO <sub>2</sub> Permeability (barrer)	CH <sub>4</sub> Permeability (barrer)	Ideal Selectivity
Blend 1	19.97	11.79	1.69
Blend 2	0.42	0.39	1.08
Blend 3	1.00	0.79	1.26
Blend 4	11.59	4.94	2.34

#### 4. Conclusions

PES/PVAc blend membranes with various polymer/solvent ratios have been developed and characterized via FESEM, FTIR, DSC as well as TGA analysis. From micro-scale, the FESEM cross-section images justified that the developed membranes were dense with varying number of micro pores. The higher polymer/solvent ratio (viscous dope solution) tends to inhibit the micro pores formation producing dependable membranes for gas separation. The interaction and miscibility between the components polymers were attainable and deduced via FTIR and DSC analysis. From TGA scan, the thermal stability of the developed blend membrane apparently lies between the parent polymers, where the addition of the more stable polymer (PES) stabilized the thermal stability of the weaker polymer (PVAc). The results suggest the applicability of the PES/PVAc blend to be developed as a membrane to push the performance of native polymeric membrane for gas separation.

#### 5. References

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