

MISCIBILITY CHARACTERISTICS OF POLY (ETHERSULFONE) (PES) HOLLOW FIBER MEMBRANES WITH CHARGED-SURFACE MODIFYING MACROMOLECULES (cSMM) FOR WATER SEPARATIONS APPLICATIONS

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Abstract. Investigation of the miscibility of the fabricated hollow fiber membranes containing polyethersulfone (PES), additives (water or Poly (vinylpyrrolidone) kollidone) and charged-Surface Modifying Macromolecules (cSMM) is elaborated. The fabricated hollow fiber membranes were successfully produced via phase inversion process using dry/wet spinning condition at extrusion rate at 2.5 cm³/min. It's revealed that the attenuated total reflection Fourier transformed infrared (ATR-FTIR) has confirmed the blending of cSMMs in PES matrix by analyzing the shifts or intensity changes spectrum of the hollow fiber membranes. In addition, the glass transition (T_g) of the membranes determined via Differential Scanning Calorimetry (DSC) also confirmed the blending formation. The results proved the existence of charge modification which is important in enhancing the performance of nanofiltration membrane for water purification process.

Keywords: Polyethersulfone; hollow fiber membranes; ATR-FTIR; DSC; surface modification

Abstrak. Kajian berkenaan kebolehlartucampuran bagi membran gentian geronggang yang mengandungi polyethersulfone (PES), bahan tambah (air atau Poly (vinylpyrrolidone) kollidone) dan makromolekul pengubahan permukaan bercas (cSMM) adalah diperjelaskan. Membran gentian geronggang berjaya difabrikasi melalui proses penyongsangan fasa menggunakan kaedah pusaran kering/basah pada kadar penyempitan 2.5 sm³/min. Didapati bahawa jumlahan Infra-merah pengubah Fourier terkecil (ATR-FTIR) mengesahkan campuran cSMM dalam matriks PES dengan menganalisis pergerakan atau perubahan keamatan spektrum bagi membran gentian geronggang. Tambahan lagi, suhu peralihan kaca (T_g) membran yang ditentukan melalui Kalorimeter imbasan pembeza (DSC) juga mengesahkan formasi campuran. Hasil kajian membuktikan kewujudan modifikasi bercas yang mana adalah penting dalam meningkatkan prestasi membran penurasan-nano untuk proses penulenan air.

Kata kunci: Polyethersulfone; membran gentian geronggang; ATR-FTIR; DSC; pengubahan permukaan

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1.0 INTRODUCTION

Attenuated total reflection Fourier transform infrared (ATR-FTIR) is an alternative to transmission mode used for infrared spectroscopy study. It is a useful technique for studies on specific interactions between polymers in miscible blends. Additionally, it is also an important tool for identifying types of chemicals from its chemical bonds (*i.e.* functional groups). Functional group is an atom or group of atoms attached in a hydrocarbon chain or ring that confers characteristic properties to the molecule as a whole [1]. Functional group is one part of an organic molecule, where most of the reactions of molecules occur. Infrared spectroscopy is one of the most common spectroscopic techniques whereby samples were positioned in the path of infrared (IR) beam and its absorption in different IR frequencies was measured. When IR radiation passes through a sample, certain frequencies of the radiation are absorbed by the molecules of the substance which lead to molecular vibrations. The frequencies of absorbed radiation are unique for each molecule which provides the characteristics of a substance. In other words, the IR detects the vibration characteristics of chemical functional groups in a sample by interact with the chemical substance causing the chemical bonds in the matter to vibrate *i.e.* stretch, contract or bend etc. The output signal is the sum of all the cosine waves which is the Fourier Transform of the spectrum. It is also called as interferogram, that contains the basic information on frequencies and intensities characteristics of a spectrum but it is not directly interpretable. Therefore, the information is mathematically converted using Fourier Transform method, and present an infrared spectrum, which plots absorbance (or transmittance) against wavenumber [2].

FTIR is usually performed in transmission mode. However, some samples were not suitable or difficult for this normal transmission. An improvement of this transmission mode is offered by the attenuated total reflection (ATR). It has an advantage for studying thick or highly absorbing solid and liquid materials, including films, coatings, powders, threads, adhesives, polymers, and aqueous samples. For bulk material or thick film, ATR requires little or no sample preparation which made it as one of the most versatile sampling tools.

In the ATR-FTIR technique, the IR beam is guided in an IR transparent crystal by total reflection as illustrated in Figure 1. ATR occurs when a beam of radiation enters from a more-dense (with a higher refractive index) into a less-dense medium (with a lower refractive index). The fraction of the incident beam reflected increases when the angle of incidence increases. All incident radiation is completely reflected at the interface when the angle of incidence is greater than the critical angle (a function of refractive index). The IR beam penetrates a very short distance beyond the interface and into the less-dense medium before the complete reflection occurs. This penetration is called the evanescent wave and typically is at a depth of a few micrometers (μm). Its intensity is reduced (attenuated) by the sample in regions of the IR spectrum where the sample absorbs.

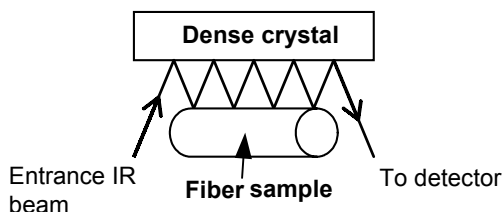


Figure 1 Schematic illustration of multiple internal reflection effect in Attenuated Total Reflectance (ATR)

ATR-FTIR spectra are equivalent to FTIR spectra, except the ATR-FTIR technique requires smaller amount sample compared with FTIR and allows precision control of samples [3]. This made the technique is rapid and simple. Not only that, the spectrum obtained is independent of the sample thickness. This is because the reflected radiation penetrates the sample to a depth of only a few microns. Hence, this method is effective to study the surface properties of sample.

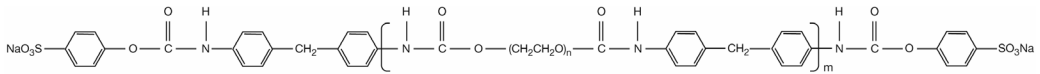
Another important polymer miscibility measurement method is Differential Scanning Calorimetry (DSC). It is applied to measure thermal transition properties of a polymer, that useful to study glass transition temperatures (T_g). Glass-transition temperature (T_g), is the thermal property which is the temperature, or range of temperatures, below which the polymer is in a glassy state and above which it is rubbery. A conventional method of thermal characterization is differential scanning calorimetry, in which the thermal property monitored is the change in enthalpy. Different compositions will effect the thermal transition and thus reflected in the T_g . Hence, the thermal characteristic of the bulk polymer is an important characteristic to demonstrate miscibility feature of a polymer blend.

Thus the objective of this study were (1) to fabricate hollow fiber membranes by utilizing Poly (Ethersulfone) which modified by blending charged-Surface Modifying Macromolecules (cSMM) and (2) to study the blending and miscibility of cSMM with PES by means of FTIR and DSC characterization methods.

2.0 EXPERIMENTS

2.1 Materials and Hollow Fiber Fabrication

All samples used in this study were home-made polyethersulfone (PES) hollow fiber membranes produced via dry/wet spinning process described elsewhere [4]. The fabricated membranes were prepared using homogenous solution that consist of polyethersulfone (PES RADEL A-300, Amoco Chemicals), *N*-methyl-2-pyrrolidone (NMP, Merck) and Poly (vinylpyrrolidone) kollidone 15 (PVPk-15, Merck), water (deionized) and charged-Surface Modifying Macromolecules (cSMM). The cSMM was laboratory synthesized which consist of Poly(ethylene glycol) PEG end-capped



Poly(ethylene glycol) PEG end-capped with Hydroxyl benzene sulfonate (HBS)

Figure 2 Chemical structures of cSMM polymers used in the fabricated hollow fiber membranes

with Hydroxy benzene sulfonate (HBS), sodium salt. The cSMM used in the hollow fiber membranes fabrication was given in Figure 2.

The PES powder was initially dried in a vacuum oven at 120 °C for 5 h to remove its moisture content. Then the dried PES was dispersed slowly as final composition after PVPk15 and cSMM, around 30-45 minutes into NMP solvent contained in a flask with a high-speed mechanical mixer stirred. After that, the mixing continued for another 8 hours to ensure the solution becomes homogenous. The homogenous polymer solution was put into an ultrasonic bath for about 2-3 h to remove the bubbles and then was kept at room temperature for 24 h before preparing for fabrication.

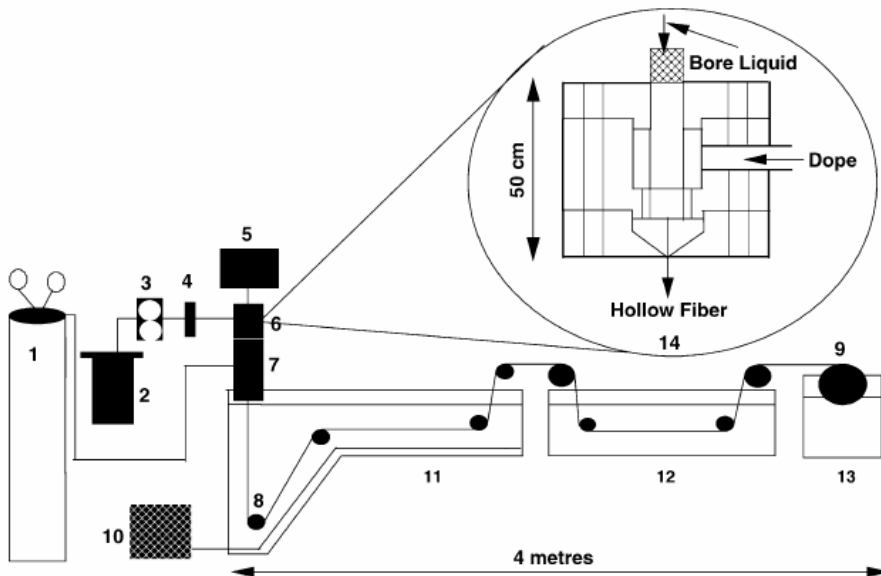


Figure 3 Schematic diagram of hollow fiber spinning system: (1) nitrogen cylinder; (2) dope reservoir; (3) gear pump; (4) on-line filter, 7 mm; (5) syringe pump; (6) spinneret; (7) forced convective tube; (8) roller; (9) wind-up drum; (10) refrigeration/heating unit; (11) coagulation bath; (12) washing/treatment bath; (13) wind-up bath; (14) schematic spinneret. Adapted from Ismail *et al.*[5]

Asymmetric hollow fiber membranes were fabricated using a dry/wet spinning process with forced convection in the dry gap as shown in Figure 3. In the spinning process, the dope solution were extruded from spinneret (spinneret dimensions: o.d. 600 μm , i.d. 300 μm) and spun without any extra drawing, which the fiber take-up speed was almost the same as its free-falling speed in the coagulation bath (or the drawing ratio was nearly a unit). As powerful coagulant, water was used both as for bore fluid to immediately solidified polymer and produce hollow at inner side of fiber and as the external coagulant to yield an outer selective dense layer. The dry-wet condition is kept constant at 5 cm air gap. Dope extrusion rates (DER) used is 2.5 ml/min.

2.2 Fourier Transform Infra Red (FTIR) Spectroscopy

The IR spectra were recorded on a Magna IR-560 (Nicolet) Fourier Transform infrared spectrometer fitted with a horizontal attenuated total reflectance (HATR) accessory called the thunderdome, which supplied by Termo Nicolet Corporation. The thunderdome is a unique single reflection HATR that utilizes a spherical ATR crystal as the sample contact surface [5]. The spherical configuration of the ATR crystal reduces the beam diameter into two, resulting in a concentration of energy to a smaller spot size. The ATR crystal allows for 'point to point' contact with the pressure tower device, with fail-safe pressure that avoids damage to the crystal surface and intensifies sample positioning.

Hollow fiber samples were mounted on thunderdome accessory jig making a point-to-point contact. Samples were placed on the horizontal face of the internal reflectance crystal where total internal reflection occurs along the crystal-sample interface. Hollow fiber samples need to be pressed against the ATR crystal to obtain good contact. Since the crystals are fairly soft and easily deformed, only a limited amount of pressure should be applied to the sample to obtain the necessary contact.

In this experiment, Germanium crystal with a transmission range of 1800 – 900 cm^{-1} was used. A background spectrum was conducted when analyzing hollow fiber samples as to eliminate instrumental and atmospheric contributions to the sample peaks i.e spectrum. This is also called as background correction to avoid the interference from carbon dioxide and water vapor. It is done by normalized the fiber sample radiation beam spectrum against the background spectrum.

2.3 Differential Scanning Calorimetry

In order to determine the miscibility of PES-additive blend, the glass transition temperature (T_g) of the polymers was analyzed with differential scanning calorimetry (Mettler Toledo DSC 822e). Samples were cut into small pieces, weighed in 6 ± 0.5 mg and placed into pre-weighed aluminum crucible. Then, the sample was heated from 25 to 250 $^{\circ}\text{C}$ with a heating rate of 20 $^{\circ}\text{C min}^{-1}$. T_g of the sample was determined as the midpoint temperature of the transition region in the heating cycle.

3.0 RESULTS AND DISCUSSIONS

3.1 Physical Properties of the Fabricated Membranes

The hollow fiber membranes were fabricated from three types of dopes formulation which are PES/NMP (22/78), PES/NMP/Water/cSMM (22/72/5/1) and PES/NMP/PVPk15/cSMM (22/72/5/1). All the three dope solutions were spun at extrusion rate of 2.5 ml/min at 5 cm air gap.

The identity and their characteristics of the fabricated membranes were shown in Table 1. The outer diameter of the fabricated hollow fiber membranes were measured using electronic digital caliper. The physical result shows that the outside diameter of the membranes was increased with addition of additives in the dope formulation. Most likely, this is due to the increase in the rate of coagulant (water) intrusion when cSMM is added. The diffusion rate increased slightly in the quaternary system compared to the binary system (PES only).

Table 1 Hollow fiber membranes physical properties

Hollow fiber membrane	Dope extrusion rate (ml/min)	Dope composition (weight percent) (%)	Fiber outside diameter (OD) μm
PES2.5	2.5	PES (22)	478
PC2.5	2.5	PES/PVPk15/cSMM (22/5/1)	488
WC2.5	2.5	PES/Water/cSMM (22/5/1)	532

3.2 FTIR Analysis

The comparison of ATR-FTIR spectra of membranes containing PES and membranes blended with PVPk15/cSMM and Water/cSMM are shown in Figure 4. The three spectra is a comparison of hollow fiber membranes that were spun at dope extrusion rate of 2.5 ml/min. The spectrum reveals the occurrence of interaction between the characteristic groups of PES and cSMM. The interactions were indicated by frequency shifts involving several characteristics groups and absorption intensity changes.

The characteristic IR absorption bands for PES at 1578 cm^{-1} is correspond to the C-H bond in the aromatic system. This area of aliphatic (C-H) stretch is very sensitive to structural effects [6]. The spectral region between 500 cm^{-1} and 1500 cm^{-1} is the fingerprint region and indicative of aromatic functional groups. Aromatic bands at 1578 cm^{-1} and 1486 cm^{-1} are characteristics for PES [7].

From the comparison of PES membrane spectra, emergence of several new bands were detected for the carbonyl group, amide C=O stretch ($1655 - 1680\text{ cm}^{-1}$), sulphonic stretching (1043 cm^{-1}) and CH_3 ($919 - 922\text{ cm}^{-1}$). Changes in absorption

intensity were found for sulfonate group stretching vibration at $1407 - 1412 \text{ cm}^{-1}$. The peak assign for amide (C-N) from PVPk15 were no longer observable in the PVPk15-PEGHBS blend spectrum, probably the intensity has been reduced and overlapped with sulfonate group vibration of PES at 1296 cm^{-1} . Similar trend were also observed by other studies [8].

The spectrum given in Figure 4 shows an emergence band of symmetric SO_3 vibration at 1045 cm^{-1} and the band assigned to the CH_3 vibration at $919 - 922 \text{ cm}^{-1}$. The intensities of these two bands increased due to the addition of PVPk15 and cSMM. However, the modification of adding 1% cSMM (PEGHBS) has reveal significant spectrum changes of sulfonic (SO_3), although at very small amount added. The peak of SO_3 was attributed by sulfonic salt of PEGHBS, found stronger or higher peak in Water/PEGHBS than the PVPk15/PEGHBS formulation.

The operation of ATR is by measuring the changes that occur in the total internal reflected infrared beam, due to the contact with the samples. Thus, this analysis indicates the occurrence of interactions and mixing of PES and additives at molecular level. The spectra shifts and intensity changes of pure PES and modified PES characteristics group could be attributed to the intermolecular interaction of the miscibility of PES and additives.

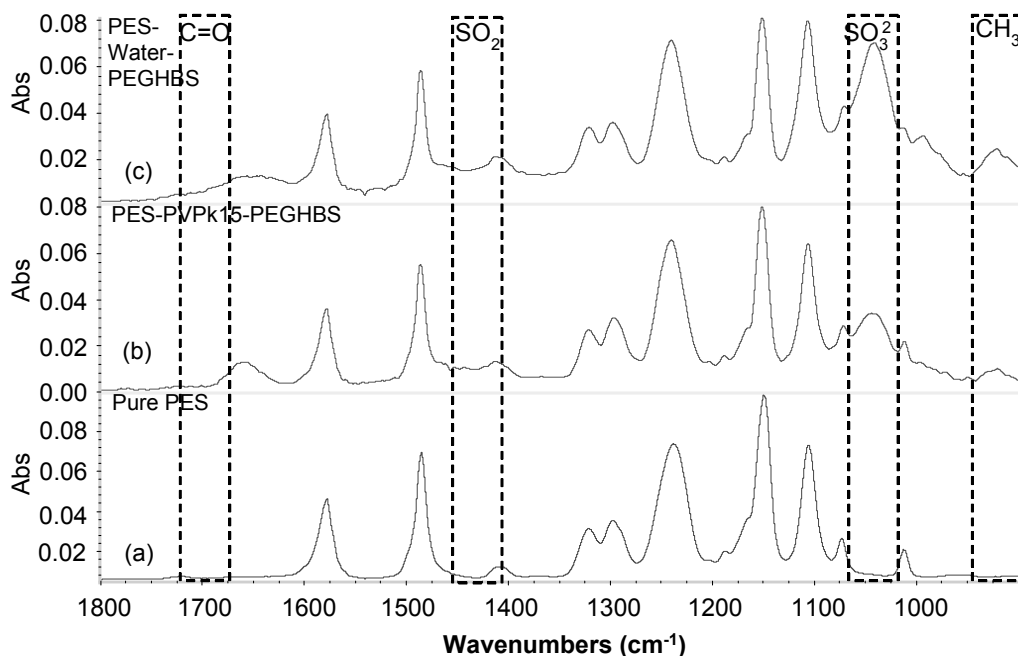


Figure 4 Infrared spectra for hollow fiber containing (a) pure PES, (b) PES-PVPk15-PEGHBS and (c) PES-Water-PEGHBS

3.3 The Glass Transition Temperature, T_g Properties of Hollow Fiber Membranes

Differential scanning calorimetry (DSC) is a well known method of thermal characterization in which the thermal property is monitored as enthalpy change. A miscible blend exhibits a single T_g whereas an immiscible blend shows multiple T_g s [9]. The midpoint T_g , given as the temperature at which half of the total change in the specific heat capacity occurs is illustrated in Figure 5. From the DSC scan, the T_g value for the unmodified PES were 231 °C. While in the blending of PEGHBS has increased T_g value of 226 °C in PES/PVP and 228 °C in PES/Water. All membranes exhibited a single T_g , which implies the homogenous blend of additive and cSMM with PES. The T_g 's of all the hollow fibers of multi-components are less than the hollow fiber of the single PES component. Compositional variation of T_g is mainly governed both by the interaction between the components and the change in chain flexibility with the compositional change [10].

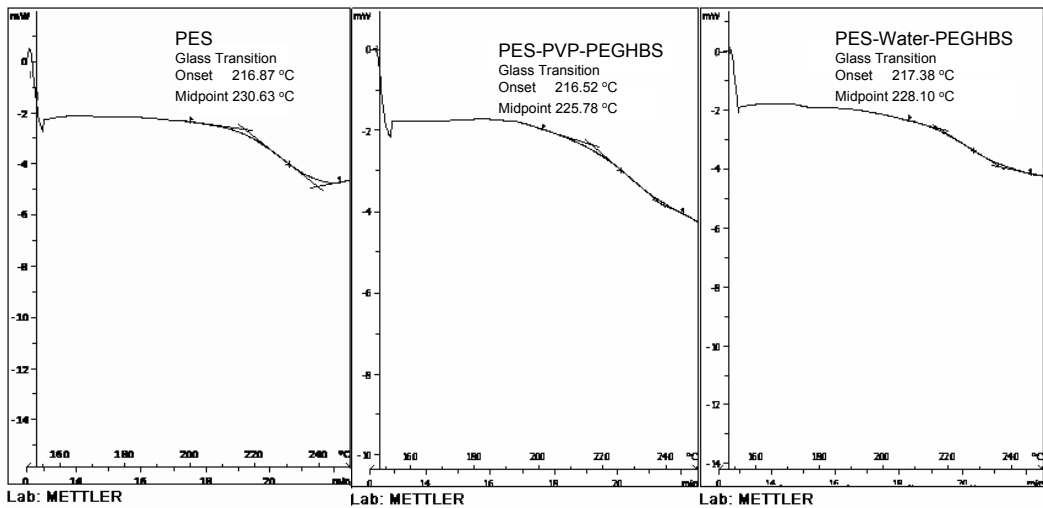


Figure 5 DSC scans of PES and modified PES by blending additives

However, the blending of 1% cSMM (PEG-HBS) has increased the T_g value. This is attributed to stronger bonds between the blend components that limit the chain mobility and increase the T_g value [11]. The blending of 1 wt% cSMM (PEG-HBS) increases T_g value by up to 6 °C for both membrane formulations, an indication of improved thermal properties and miscible polymer pairs of the modified membranes.

4.0 CONCLUSION

Polymeric hollow fibre membranes were fabricated by wet-phase inversion technique. Three types of polyethersulfone of 22% weight concentration added with Polyvinylpyrrolidone (PVPk15) or Water and charged-Surface Modifying Macromolecules PEG end-capped with Hydroxyl benzene sulfonate (HBS) were formulated. By using the attenuated total reflectance technique, spectral shifts were detected at blending membranes of PES with cSMM, though very low concentration of cSMM added. The miscibility interaction at thermal level of combination of PES and cSMM has been observed from this study, which further confirmed using Differential Scanning Calorimetry (DSC). Thus the study concludes that, DSC and attenuated total reflectance technique is relatively sensitive and practical, as far as routine-type methods are concerned. ATR spectra with reasonable signal-to-noise ratios can be easily obtained. The technique is rapid, simple and required very little sample preparation. Also, one of the major advantages of the ATR technique is that the spectrum obtained is independent of the sample thickness. Typically, the reflected radiation penetrates the sample to a depth of only a few microns. In consequence, the method is particularly useful for surface analysis of many materials. This paper has briefly described the analysis of PES polymers blending with additives using internal reflectance method. Many more exciting applications for ATR/FTIR spectrometry can be found.

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