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EFFECT OF DIFFERENT SOLVENT ON ASYMMETRIC POLYSULFONE (PSF) MEMBRANES FOR CO₂/CH₄ SEPARATION

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ABSTRACT

The asymmetric membranes solution were developed for CO₂/CH₄ separation by mixing polysulfone (PSf) with N-Methyl-2-pyrrolidone (NMP). A volatile solvent, Tetrahydrofuran (THF) was introduced into the casting solution by various loading (0 to 75%) to form a high gas separation performance of asymmetric membranes via dry/wet phase inversion method. The produced membranes were characterized using Scanning Electron Microscopic (SEM), Fourier Transform Infrared Spectroscopy (FTIR) and gas permeability test. SEM images of a membrane with NMP as a solvent has the thickest dense layer while a membrane with THF as a solvent has the thinnest thickness of the membrane. FTIR results indicating the present of sulfur dioxide (SO₂) and methyl (CH₃) group at wavelength 1170 cm⁻¹ and 2969 cm⁻¹ respectively verifying the use of PSf as a polymer. As for gas permeation test, the used of THF as a solvent shows the highest CO₂/CH₄ selectivity with the lowest permeability.

KEYWORDS

Gas separation, Volatile solvent, Tetrahydrofuran, Polysulfone.

1. INTRODUCTION

A separation process is used to transform a mixture of substances into two or more distinct products that differ from each other in composition [1]. Methods of separations include distillation, adsorption, absorption, cryogenics and membranes. Among these separation techniques, membrane-based gas separation has received considerable attention. In membrane-based gas separation process, components are separated from their mixtures by differential permeation through membranes. A number of advantages including low capital and operating costs, lower energy requirements and ease of operation are offered by membrane separation. With the development of new technologies and discovery of new materials, membrane-based gas separation has evolved to a broader field with applications. Current applications of membrane-based gas separation include oxygen and nitrogen enrichment, natural gas separation and removal of volatile organic compounds from effluent streams [2]. Among these applications, CO₂ removal from methane gas is gaining popularity nowadays. A number of articles were published by different researchers aimed at reporting various technologies for recovery and separation of CO₂ [3]. Conventionally, technologies include absorption and adsorptions are used for CO₂ separation. Nevertheless, few circumstances encountered by these conventional technologies included high-energy consumption, unit operation complexity and equipment corrosion problem urge the needs to converse to new separation technology.

Owing to the limitations brought by conventional technologies, membrane technologies become a potential alternative for gas permeation and separation. The type of common organic membranes widely studied for gas permeation and separation is polymer membranes due to its low cost and relatively easier preparation. However, the application of polymer membranes is limit by its low chemical and thermal resistance as well as low mechanical strength.

It is also known that the properties of solvent affect the morphology and performance of the membrane. For example, addition of a volatile solvent into a polymeric solution, along with a non-solvent, can change liquid-

liquid demixing behavior, and as a result can cause a change in the membrane morphology and performance. Besides, adding a co-solvent to a polymeric solution can eliminate macro-void formation during instantaneous demixing and change the morphology of the membranes from finger-like to sponge-like structure despite of instantaneous demixing [4]. During membrane synthesis, the choice of polymer in membrane preparation is very important as it influences the ultimate membrane properties. The most commonly used commercial polymers for gas separation are the phenyl group-based polysulfone (PSf), polyethersulfone (PES) and aromatic polyimide. PSf was selected as membrane materials because of commercial availability, processing ease and favourable selectivity-permeability characteristics.

A formation of asymmetric membrane does not only depends on type of polymer but also the selection of suitable solvent is important in asymmetric membranes structure and separation performance. For water soluble solvents used, the most common solvent is N-methyl-2-pyrrolidone (NMP) which has a high solvent power for PSf and low toxicity and is completely miscible with water, alcohols and organic acids.

Recently, Aroon et al., 2010 investigated the effects of co-solvent additives on the morphology and gas permeation properties of polysulfone membranes [4]. The data showed that the addition of tetrahydrofuran (THF), a volatile solvent to the PSf/NMP solution increased the gas selectivity of the membrane. It should be noted that THF is miscible with water and that polysulfone is highly soluble in THF. Thus, in this research, the PSf asymmetric flat sheet membranes were fabricated to investigate the effect of different solvent for CO₂/CH₄ gas separation.

2. EXPERIMENTAL

2.1 Materials

Polysulfone (PSf) was purchased from Amoco Chemicals was dried at 70°C overnight before use. N-Methyl-2-pyrrolidone (NMP) with a purity of 99.5% was purchased from Merck while Tetrahydrofuran (THF) with 72.11 g/mol molecular weight (MW) was purchased from QREC (ASIA)

and were used without further purification. Tap water was used as the coagulation bath medium.

2.2 Preparation of Dope Solutions

Briefly, three types of asymmetric PSf flat sheet membranes dope solutions were prepared by dissolving 25 wt/v% polysulfone and 75 wt/v% different composition of solvent as tabulated in Table 1.

Table 1: Composition of Dope Solutions

Samples	PSF (wt/v%)	Solvent	
		NMP%(wt/v)	THF%(wt/v)
PSF 1	25	75	0
PSF 2	25	0	75
PSF 3	25	37.5	37.5

After 24 hours of stirring and PSf had completely dissolved, the solutions were removed and sonicated for 30 minutes to remove any trapped bubbles.

2.3 Fabrication of Flat Sheet Membranes

In order to prepare asymmetric PSf flat sheet membranes through manual casting using dry/wet phase inversion method, the dope solutions were casted manually on a clean glass plate using glass rod. The cast sheet was left for two minutes for solvent evaporation. After 2 minutes, the cast sheet together with the glass plate was immersed in the coagulation bath (tap water). The cast sheet was left in the tap water until it solidified and peels off from the glass plate. Then, the membrane was transferred into fresh water and kept 1 day to remove the residual solvent completely. Finally, the membrane was dried for 24 hours in the ambient atmosphere.

2.4 Characterization

2.4.1 Morphology structure by SEM

The surface morphologies of asymmetric PSf membranes were investigated using Scanning Electron Microscopy (SEM). Image of skin layer structure and cross sections of membranes prepared under different composition were obtained.

2.4.2 Functional group by FTIR analysis

The functional groups present in asymmetric PSf membranes were identified using ATR-FTIR spectrometer. The samples were scanned by single-reflectance ATR accessory with IRTRACE-100. The samples were prepared by cutting it into a small pieces and scanning at a wavelength 400 cm⁻¹ to 4000 cm⁻¹.

2.5 Gas Separation Performance by Gas Permeation System

The separation performance of PSf asymmetric membranes on CO₂ removal were conducted by studying the coefficient of permeability and selectivity. Gas permeation system was used to evaluate the membrane gas separation performance using pure CO₂ and CH₄. Gas permeation rates were measured by a soap bubble flow meter. Gas permeation rate was calculated [5]:

$$(P/D)_i = Q_i / \Delta P \quad (1)$$

(P/D)_i is pressure-normalized flux or permeability for gas i (GPU); Q_i is volumetric flow rate of gas i; ΔP is pressure difference across membrane;

A is membrane effective surface area; l is membrane skin thickness Selectivity (unitless) was determined [5]:

$$\alpha_{ij} = P_i/P_j = (P/D)_i/(P/D)_j \quad (2)$$

3. RESULTS AND DISCUSSION

3.1 Effect of Different Solvent on Asymmetric Polysulfone Membrane Properties

3.1.1 Surface morphologies of polysulfone membrane

Morphological structures of asymmetric PSf flat sheet membrane were analyzed by SEM to illustrate the effect of different solvent towards the morphologies of the prepared membrane. Based on the result, it indicates that PSf membranes prepared from different THF composition had variety structure and various thicknesses.

In general, the skin layer thickness affected the separation performances of membranes. In addition to the membrane formation, the evaporation step such as evaporation time prior to immersion in the coagulation bath during the dry/wet phase inversion technique also influences the thickness of the membrane. A longer evaporation step generally leads to a thicker membrane while a shorter evaporation time results in a thinner skin layer and it can affect separation performance [4]. Therefore, presence of a volatile solvent such as THF and less volatile solvent such as NMP in the casting dope can affect solvent evaporation rate as well as skin formation during dry phase inversion [5].

Based on Figure 1, SEM images show the thickness of the membrane for PSf 1, PSf 2 and PSf 3 were 62.0 μm, 20.2 μm and 79.7 μm respectively. According to a study, membrane cast from a dope where NMP/THF mixture was used instead of NMP along has a thicker skin layer [4]. PSf 3 has the thickest skin layer compared to other as it is cast from a dope where NMP/THF mixture was used as a solvent. For PSf 2, although the thickness of the membrane is the thinnest but the membrane shows a defect-free surface.

Based on Figure 2, it shows surface morphologies of PSf membranes. The surface layer of PSf 1 and PSf 3 membrane show that pinholes appeared sparsely on the membrane surface while PSf 2 membrane shows that the surface was smooth with no clear pores. PSf 3 with the thickest skin layer shows a small amount of pinholes on the surface compared to PSf 1. The thicker skin layer enables the fabrication of membranes with less defects and pin-holes. In the previous study of super selective PSf membranes, a volatile solvent can rapidly evaporate from the outermost surface of the membrane which causes the polymer-rich phase to undergo rapid vitrification and hence an oriented membrane skin with few pores or defects will be formed [6].

Besides, adding a co-solvent to the dope solution (THF into the polymer-NMP solution system) can eliminate macro-void formation during instantaneous demixing and change the morphology of the membranes from macro-voidal to sponge-like structures despite instantaneous phase demixing [7].

Based on Figure 3, the morphology of PSf 1 membrane was porous with a thick dense layer. This membrane can be divided into three part of layers, each with different structures. The top layer consist of thick dense layer with no porous structure but as the layers goes down, the dense layer become thinner and porous structure starts to build. At bottom of membrane, the structure is thin with thick sponge-like porous structure. In previous study of fabrication PSf by Idris et al. reveals the similar morphological structures [8].

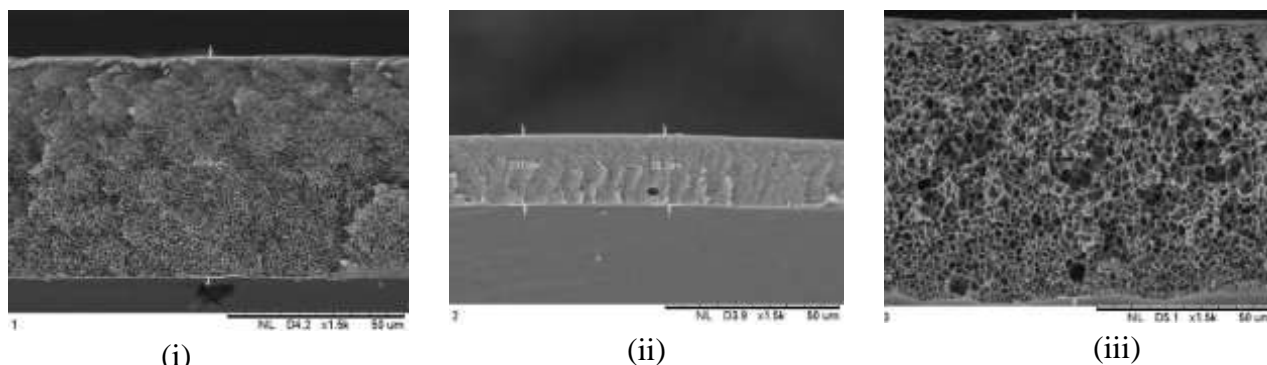


Figure 1: SEM images of PSf membranes thickness at 1500X magnification (i) PSf 1 (ii) PSf 2 and (iii) PSf 3

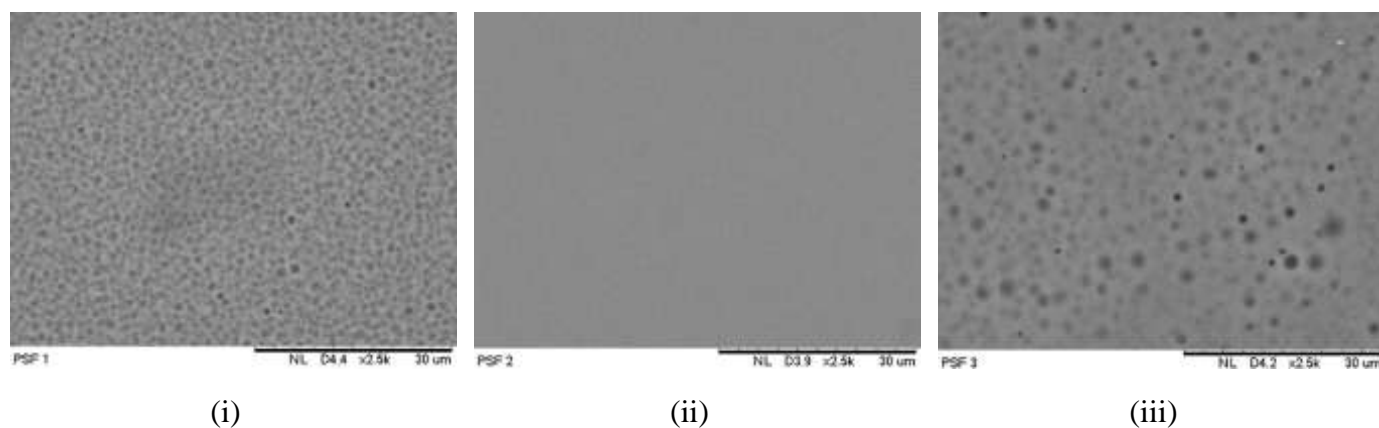


Figure 2: SEM images of PSf membranes surface layer at 2500X magnification (i) PSf 1 (ii) PSf 2 and (iii) PSf 3

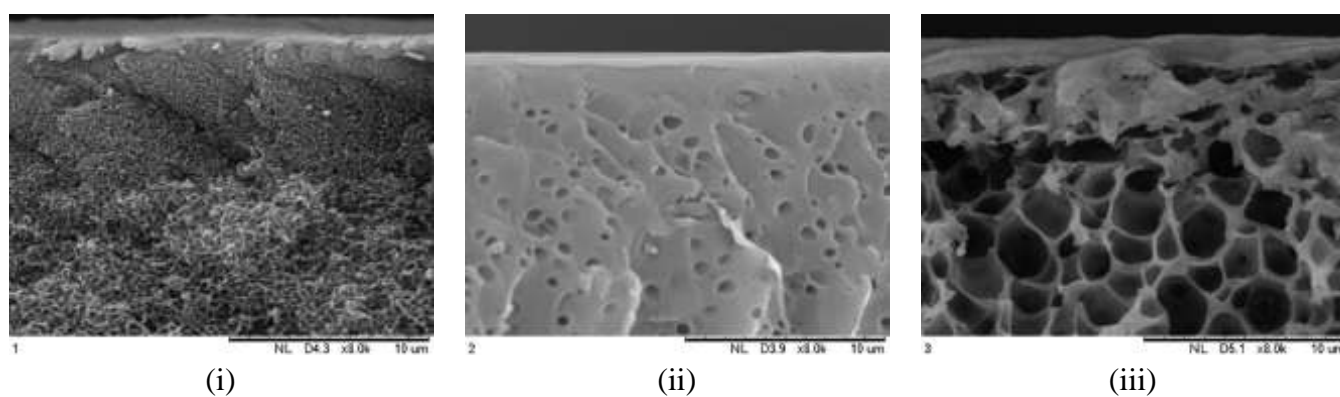


Figure 3: SEM images of PSf membranes cross section at 3000X magnification (i) PSf 1 (ii) PSf 2 and (iii) PSf 3

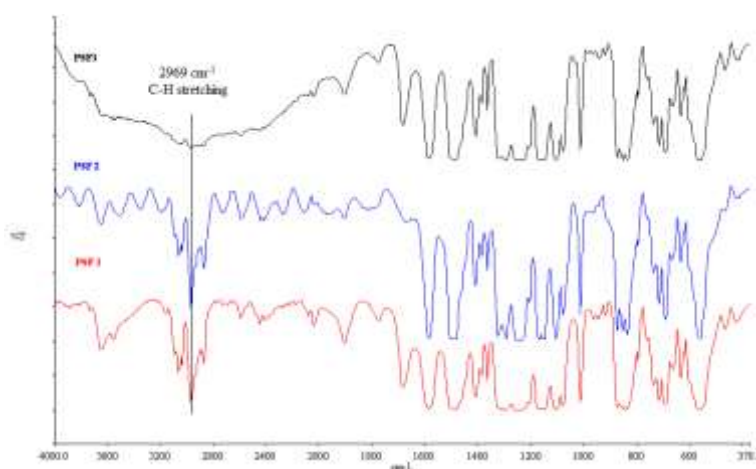


Figure 4: FTIR Spectra of PSf Membranes

The porous substructure provides the thin membrane with strength and durability which prevents membrane destruction by pressure and temperature. By phase inversion, thin layer of polymer solution is immersed into a coagulation bath for solvent exchange between solvent and nonsolvent (water) to form asymmetric membranes. The phase separation occurs during the solvent exchange process, resulting desired porous structure [9].

For PSf 3, the SEM result is shown in Figure 3(iii). The PSf 3 membrane morphology is generally similar to that of the membrane cast from a dope without THF (Figure 2(i)) in term of dense layer and sponge-like porous structure. This membrane only consist of two part of layers with dense layer on top of the membrane and porous structure at the bottom of the membrane. In PSf 3, dense layer is thin with thicker and larger porous structure compared to PSf 1. According to Vriezolk, Nijmeijer and de Vos, 2016, membrane cast from a dope where NMP/THF mixture was used is denser than the membranes that were fabricated with THF in the polymer solution [10].

The formation of finger-like macro-voids diminished and the macro-voids became much shorter in Figure 3(ii). When using pure THF as solvent (sample PSf 2), a teardrop type macrovoids can be found and their sizes decrease with an increase in THF content. Whereas, the pore size in the microporous substructure increases with an increase in the THF content. Empirically, it has been pointed out that the formation of macrovoid structure in a flat membrane can be avoided if the phase inversion process undergoes a slow precipitation rate of polymer or delayed L-L demixing process [11]. Therefore, more the THF the more delayed L-L demixing it will become, and the macrovoid structure diminishes gradually.

3.2.2 Chemical functional group analysis by FTIR

Figure 3 shows the FTIR spectra for PSf membranes based THF of 0wt/v%, 75wt/v% and 37.5wt/v%. The absorption of PSf membranes were determined in wavelength of 400 to 3000 cm^{-1} . The original PSf molecule consist of functional groups such as sulfur dioxide (SO_2) and methyl (CH_3) group [12]. From Figure 4, the wavelength of 1170 cm^{-1} and 2969 cm^{-1} representing SO_2 and CH_3 group respectively inside of PSf. Based on

previous research, S=O and C-H stretching exist in wavelength 1150 cm⁻¹ and 2870 cm⁻¹ indicating SO₂ and CH₃ group respectively [13].

In contrary, different trends of spectra were observed when the casting solution prepared by different weight/volume percentage of THF. For 0wt/v% of THF, there were bands at 1685 that corresponding to C=O. Based on previous research, C=O exists in wavelength 1670 cm⁻¹ indicating carboxyl groups [14]. For 75wt/v% of THF, there was band at 1645 cm⁻¹ that indicated for the O-H band. Based on previous research, O-H stretching exists near wavelength 1640 cm⁻¹ indicating O-H band from water [15]. For 37.5wt/v% of THF, there were bands at 1589 cm⁻¹ is related with the benzene ring stretching mode. Based on previous research, strong reflectance in 1588-1 is related with the benzene ring stretching indicating aromatic ring vibrations [9].

3.3 Gas separation performance

Separation performances of membrane were tested in gas permeation system. Single feed gases were used by passing through a flexible hose before feeding it to the membrane module. A flat sheet membrane was employed in this study. A membrane with diameter of 3.7 cm was mounted between the permeate chamber and the feed gas chamber supported by a porous metal disk and sealed with rubber O-rings. The permeation rate was measured by a bubble flow meter. Three different PSf asymmetric flat sheet membrane named as PSf 1, PSf 2 and PSf 3 were prepared based on composition of three casting solutions developed as listed in Table 4.1 were exhibit a clear difference on the CO₂/CH₄ separation performance as shown in Table 4.2.

Table 1: Permeability and selectivity of carbon dioxide (CO₂) and methane (CH₄)

Membrane Name	Permeability (GPU)		CO ₂ /CH ₄ Selectivity
	CO ₂	CH ₄	
PSf 1	58.14	70.31	0.83
PSf 2	14.14	9.26	1.53
PSf 3	13.65	12.38	1.10

The permeation of CO₂ and CH₄ in PSF membranes with different weight/volume percentage 0wt/v%, 75wt/v% and 37.5wt/v% of THF were investigated at ambient temperature and the feed gas pressure of 4 Bar. As shown in Table 4.2, PSf 1 show the highest permeability of carbon dioxide and methane at 58.14 GPU and 70.31 GPU respectively with the lowest selectivity of CO₂/CH₄. The highest permeability for both CO₂ and CH₄ can be attributed due to thinner skin layer while lowest selectivity due to surface defect with pin-hole.

PSf 2 gives the highest CO₂/CH₄ selectivity of 1.53. The permeability of CO₂ is in the middle between the PSf 1 and PSf 3 while the permeability of CH₄ is the lowest among the three membrane. By using THF as solvent thus increased the selectivity of asymmetric PSf mainly attributed to relatively defect-free skin layer.

PSf 3 gives average results with CO₂/CH₄ selectivity of 1.10. The permeability of CO₂ is the lowest among the three membrane while the permeability of CH₄ is in the middle between the PSf 1 and PSf 2. In general, a membrane with higher selectivity and lower permeability will be formed when the volatile solvent concentration is increased in the polymer solution.

4. CONCLUSION

In this present work, PSf asymmetric flat sheet membrane for gas separation have been developed. Three different casting solution were chosen as a solvent with fixed the concentration of the component. While in the final stage, Scanning Electron Microscopy (SEM) was used to examine the membrane morphology. The result showed the different type of membranes cross-section and membrane surfaces were obtained from different casting solution formulations. The mechanisms of chemical structure were investigated by Fourier Transform Infrared (FTIR). There is a trend that seemed to indicate chemical structure of functional group as a different molecular structure in the different solvent.

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REFERENCES

- [1] Adatoz, E., Avci, A.K., Keskin, S. 2015. Opportunities and challenges of MOF-based membranes in gas separations. *Separation and Purification Technology*, 152, 207-237.
- [2] Chung, T.S., Jiang, L.Y., Li, Y., Kulprathipanja, S. 2007. Mixed matrix membranes (MMMs) comprising organic polymers with dispersed inorganic fillers for gas separation. *Progress in Polymer Science*, 32 (4), 483-507.
- [3] Chew, T.L., Ahmad, A.L. 2016. Gas Permeation Properties of Modified SAPO-34 Zeolite Membranes. *Procedia Engineering*, 148, 1225-1231.
- [4] Aroon, M.A., Ismail, A.F., Montazer-Rahmati, M.M., Matsuura, T. 2010. Morphology and permeation properties of polysulfone membranes for gas separation: Effects of non-solvent additives and co-solvent. *Separation and Purification Technology*, 72 (2), 194-202.
- [5] Ismail, A.F., Lai, P.Y. 2003. Effects of phase inversion and rheological factors on formation of defect-free and ultrathin-skinned asymmetric polysulfone membranes for gas separation. *Separation and Purification Technology*, 33 (2), 127-143.
- [6] Ismail, A.F., Dunkin, I.R., Gallivan, S.L., Shilton, S.J. 1999. Production of super selective polysulfone hollow fiber membranes for gas separation. *Polymer*, 40 (23), 6499-6506.
- [7] Albrecht, W., Weigel, T., Schossig-Tiedemann, M., Kneifel, K., Peinemann, K.V., Paul, D. 2001. Formation of hollow fiber membranes from poly (ether imide) at wet phase inversion using binary mixtures of solvents for the preparation of the dope. *Journal of Membrane Science*, 192 (1-2), 217-230.
- [8] Idris, A., Man, Z., Maulud, A., Khan, M. 2017. Effects of Phase Separation Behavior on Morphology and Performance of Polycarbonate Membranes. *Membranes*, 7 (2), 21.
- [9] Jiang, L.Y., Chung, T.S., Kulprathipanja, S. 2006. An investigation to revitalize the separation performance of hollow fibers with a thin mixed matrix composite skin for gas separation. *Journal of Membrane Science*, 276 (1-2), 113-125.
- [10] Vriezokolk, E.J., Nijmeijer, K., de Vos, W.M. 2016. Dry-wet phase inversion block copolymer membranes with a minimum evaporation step from NMP/THF mixtures. *Journal of Membrane Science*, 504, 230-239.
- [11] Shieh, J.J., Chung, T.S. 1998. Effect of liquid-liquid demixing on the membrane morphology, gas permeation, thermal and mechanical properties of cellulose acetate hollow fibers. *Journal of Membrane Science*, 140 (1), 67-79.
- [12] Daramola, M., Hlanyane, P., Sadare, O., Oluwasina, O., Iyuke, S. 2017. Performance of Carbon Nanotube/Polysulfone (CNT/Psf) Composite Membranes during Oil-Water Mixture Separation: Effect of CNT Dispersion Method. *Membranes*, 7 (1), 14.
- [13] Voicu, S.I., Gales, O., Nechifor, G., Nechifor, A.C. 2011. Polymer coat improves the detection ability of sensing enzymes.
- [14] Geng, Y., Li, J., Jing, X., Wang, F. 1997. Interaction of N-methylpyrrolidone with doped polyaniline. *Synthetic Metals*, 84 (1), 97-98.
- [15] Tu, C.W., Kuo, S.W. 2014. Using FTIR spectroscopy to study the phase transitions of poly(N-isopropylacrylamide) in tetrahydrofuran-d₈/D₂O. *Journal of Polymer Research*, 21, 476.