

ELEVATED H₂/N₂ SEPARATION PERFORMANCE BY ANNEALING POST-TREATMENT OF POLYSULFONE HOLLOW FIBER MEMBRANE

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ABSTRACT

This study aims to enhance the H₂/N₂ separation performance of polysulfone (PSF) hollow fiber membranes by annealing. X-ray diffraction, SEM, and FESEM were utilized to evaluate morphological and structural changes in denser annealed PSF membranes. AFM topography images were used to investigate the annealed form and roughness of PSF membranes. Before testing membrane permeation, it was annealed at 120, 150, and 190 °C to optimize gas separation performance. Compare to all annealing temperatures (120, 150, and 190 °C), the annealed PSF membrane at 150 °C had the greatest H₂/N₂ selectivity (16.18), but its separation performance was unsatisfactory since it was below the Robeson upper limit curve. The PSF before annealing and the PSF annealed at 190 °C showed outstanding separation performance (2.60 and 2.71, respectively), despite their lower selectivity than the PSF annealed at 150 °C.

Keywords: Polysulfone, Polymer Membrane, Selectivity Enhancement, Gas Separation, Annealing Treatment.

RASĀYAN J. Chem., Vol. 15, No.4, 2022

INTRODUCTION

Hydrogen could be utilized as promising renewable energy, however, it must first be separated from other compounds (such as H₂/N₂ gasses mixtures) during the production process.¹ Among other separation methods, membrane technology was the most efficient method of separating hydrogen from this gas mixture due to its low energy consumption, simple processes, a pretty small expense, and commitment to combating climate change.²⁻⁵ Polymeric membranes were the very frequently utilized membrane type in industry sectors owing to their inexpensive production cost,⁶⁻⁸ as well as their selectivity for hydrogen.⁹⁻¹³ Polysulfone (PSF) was selected because of its satisfactory gas permeability, high selectivity, moderate cost, and widespread commercial use.¹⁴⁻¹⁶ As a result of the foregoing, PSF was identified as an appropriate glassy polymer for the fabrication of H₂ separation membranes.¹⁷ However, the performance of polymeric membranes for gas separation demonstrates a reverse association between selectivity and permeability.¹⁸

Polymeric membranes, in general, have high permeability, but poor selectivity.¹⁹ Annealing treatment could improve selectivity.¹⁴ Annealing is often used to cure poor adhesion between polymer and zeolite defects by retaining the flexibility of the polymer chain.²⁰ For example, heat treatment could raise the H₂/CH₄ selectivity of co-polyimide membrane up to 136.73%.²¹ Previously, annealing membrane at 150 °C could increase the selectivity of H₂/C₃H₈ by 619.77% (from 3.08 to 22.19).¹⁶ Moreover, the annealing temperature had an effect on the membrane characteristics, specifically, a greater temperature may boost the mobility of polymer chains by increasing the solid surface's affinity.²² Thus, this work performs

annealing on PSF membranes at different temperatures (120, 150, and 190 °C) to achieve the increasing of H₂/N₂ gas separation performance by adjusting the polymer chain flexibility of PSF membrane.

EXPERIMENTAL

Material

Preparation of PSF hollow fiber membrane can be found elsewhere.^{11,16,23} PSF membranes were used for the annealing treatment. In addition, gas permeation tests utilized several materials as follows: epoxy resin, cotton, PSF membranes after annealing treatment, H₂ gas (99.99% H₂, ultra-high purity), and N₂ gas (99.99% N₂, ultra-high-purity).

Post-treatment Membrane Methods

PSF membranes were linked to a module assembled and wrapped with aluminum foil; the module comprised of three tiers, which had twenty membranes each measuring 0.2 m in length. Following this, the PSF membranes were annealed for 1 hour in a vacuum muffle furnace at a heating rate of 0.3 °C/min. The annealing process was carried out at temperatures ranging from 120, 150, and 190 °C.

Membranes Characterization

At 40 kV, X-ray diffraction (XRD Rigaku, SmartLab) was employed measuring the PSF intermolecular width alteration (d-spacing). In addition, scanning electron microscopy (SEM VE-8800, Keyence) at 5 kV was used to observe the PSF membrane morphologies. Further analysis of the chosen PSF membranes was performed using FESEM (JEOL, JSM-7610F). Furthermore, the roughness surface film morphology was observed using atomic force microscopy (AFM, Seiko, SPA400 DFM). The topographic pictures monitored in the tapping mode using AIST-NT software.

Post-treatment Membrane Methods

Five 0.1 m membranes were potted into a glass cylinder prior to performing the gasses permeance evaluation. The modules were tested with a single gas of H₂ and N₂ at 25 °C and 2 bars input pressure. Gas permeance experiments were conducted using bubble flow or pressure gradient, according to the number of permeance values. It was related to the detection limit. The bubble flow procedure was used if the permeance result was greater than 10⁹ mol/(Pa m² s¹). The differential pressures approach was used to examine membranes for a lower permeance value (<10⁹ mol/(Pa m² s¹)).²⁴ Fig.-1 displayed the gasses testing setup.

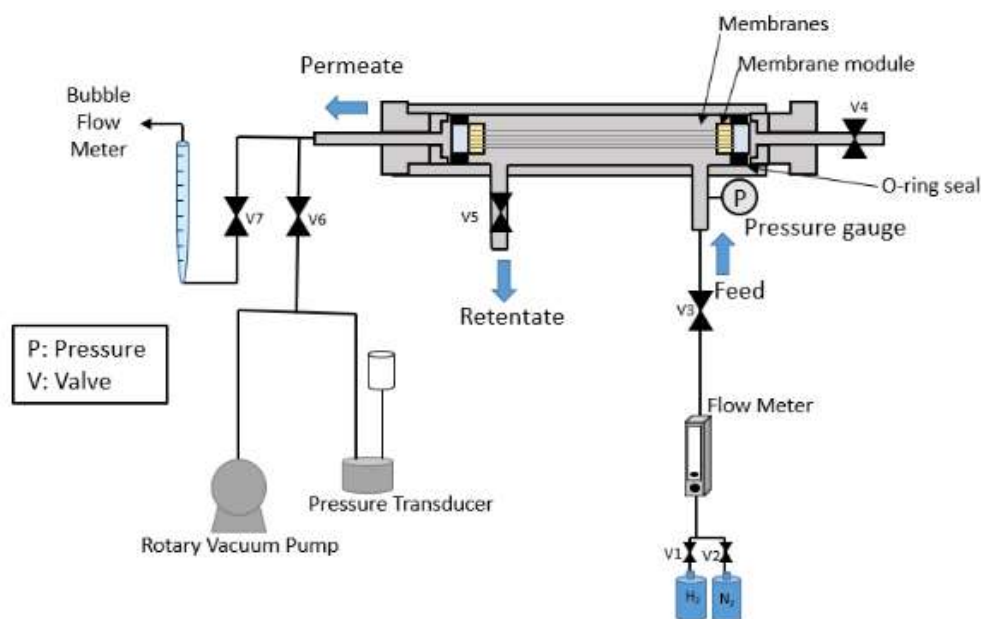


Fig.-1: Gas Testing Setup Design

RESULTS AND DISCUSSION

Microstructure Analysis

Fig.-2 exhibited a structural change in the polymer after the annealing treatment was noticed as a shift in the characteristic PSF diffraction peak. Diffractograms of the PSF revealed an amorphous phase. Although PSF lacks the sharp peak characteristic of crystalline material, d-spacing could still be estimated due to PSF's crystalline characteristics and poor crystallinity.²⁵ The d-spacing in this PSF corresponded to the intersegmental width among polymer chains.²⁶ In advance of annealing, the unmodified membrane exhibited a more defined peak. However, following treatment, the membranes' peaks expanded and shifted to the right. The large peaks suggested that annealing reduced PSF's crystallinity. In addition, annealing lowered the polymeric chain's flexibility, as shown by the 2θ shift. This decline in chain flexibility exhibited that the polymer matrix was denser, as seen by the d-spacing reduction. However, when the annealing temperature rose, the d-spacing reduction was modest, because the treatment did not appreciably alter the structure of the polymer.

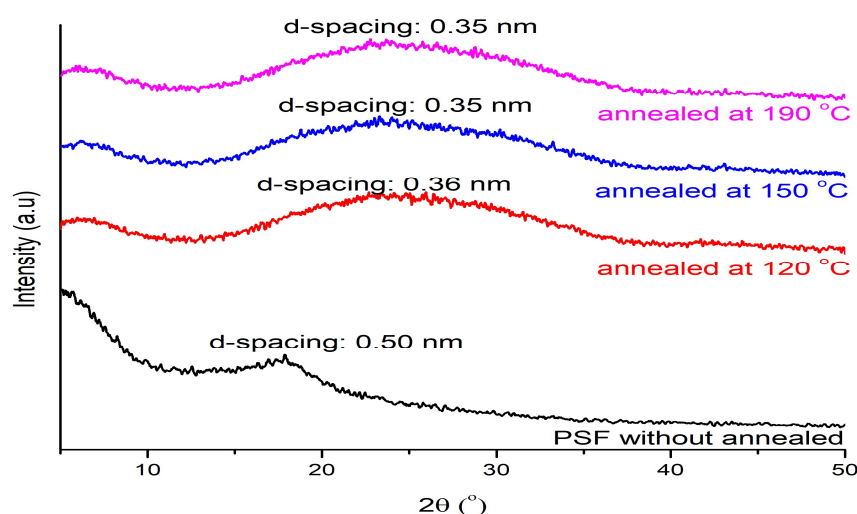


Fig.-2: XRD Diffractogram of PSF Membrane With or Without Annealed

Morphological Observation

The cross-section morphologies upon the modified membranes were exhibited in Fig.-3, while SEM observation of unmodified membrane have been exhibited by Wijiyanti *et al.*²³. The morphological image was comparable to previous research published by Tsai *et al.* indicating that the heat treatment procedure effectively increased the matrix densities.²⁷ The higher density polymer matrix contributed from the changing polymer chain flexibility due to the affinity of the solid surface enhance.²² It was predicted that improving polymer characteristics would increase membrane performances. Table-1 demonstrated the thickness of annealed PSF membranes. Although the morphological alterations were not entirely obvious, these findings corroborate the XRD investigation, which revealed that no substantial change in the d-spacing number occurred either.

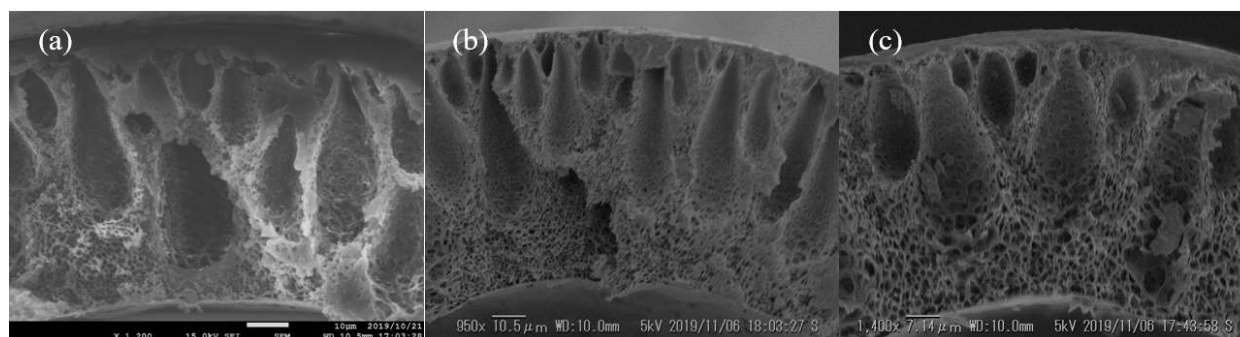


Fig.-3: SEM Picture of Modified Membranes That Have Been Annealed at (a) 120; (b) 150; and (c) 190 °C

Table-1: Dense Layer Thickness on the Annealed PSF Membranes

Membrane	Dense layer thickness (μm)
PSF annealed at 120°C	6.14
PSF annealed at 150°C	6.07
PSF annealed at 190°C	5.06

Roughness Analysis

AFM characterization was performed to determine how the annealing process changed the membrane surface. Fig.-4 is demonstrated three-dimensional and planar AFM pictures. Prior to the annealing process, the PSF membranes had a rougher structure than the annealed PSF membranes, as the latter's structure became smoother and more flexible as a result of the polymer solid surface's increased affinity, from 5.400 to 2.927 nm of mean roughness. The findings of the AFM analysis corroborate those of the XRD and SEM examinations. The roughness of the surface of the PSF membranes may have facilitated penetration.²⁸

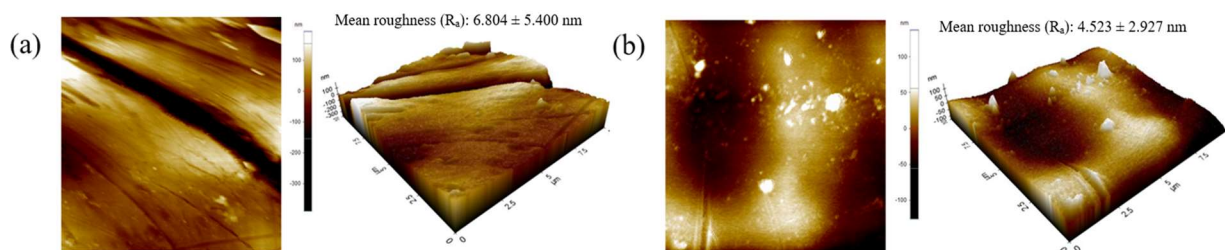


Fig.-4: AFM of the: PSF membrane (a) Without Annealing and (b) Annealed at 190°C

Gas Permeation Evaluation

As indicated in Fig.-5, the permeance of H_2 and N_2 and the selectivity of H_2/N_2 were utilized to determine the separation performance of unmodified and modified membrane by annealing. In advance of heat treatment, unmodified membrane exhibited the high permeation, but a poor selectivity. For the unmodified membrane, Knudsen diffusion occurred since the membrane selectivity neared Knudsen selectivity.²⁹ Unlike the PSF annealed at 120 and 150 °C, both membranes showed a 99% permeability decrease for all gases. Because the bubble flow technique could not be utilized to determine the drastically decreased gas penetration, the pressure difference approach was employed. The permeation decrease was inversely related to selectivity, the PSF annealed at 120 and 150 °C enhanced H_2/N_2 selectivity by 508 and 522%, respectively. This occurred because the membrane structure became denser, as reported by decreasing in d-spacing. Narrowing depreciation pores slowed the passage of N_2 gas across the polymer chain. This results was relevant with the research published by Tsai *et al.* who investigated annealing polyacrylonitrile hollow fiber membranes at temperatures of 120 and 150 °C.²⁷ Although the ideal selectivity value did not meet Knudsen selectivity, the diffusion process on the membrane was almost identical to Knudsen diffusion, which is happened when the membrane pore size was more than the size of the gas molecules, but less than their mean free path.³⁰ The intermolecular width (d-spacing) among the polymer layers in the membranes is considered to reflect the nanochannel pore size in the membrane employed for the gasses diffusion route, while H_2 and N_2 diameter molecules were 0.289 and 0.364 nm.³¹ The difference observed that the free volume of the PSF annealed at 120 and 150 °C was decreased, which resulted in the selectivity enhancement, in accordance with research results published by Dong *et al.*³² Unlike in the case of the PSF annealed at 190 °C above T_g (186 °C), the gas permeation was reduced, but no more than that for the PSF annealed at 120 and 150 °C, i.e., 46 and 48% for H_2 and N_2 , respectively. The negligible decrease in gas permeation across the membrane was caused by the polymer structure becoming denser and more flexible, as seen by the cross-section morphology (Fig.-3(c)). Furthermore, the PSF annealed at 190 °C increased the H_2/N_2 selectivity by 4%, which was smaller than the PSF annealed at 120 and 150 °C. The membrane diffusion mechanism was identical to the unmodified membrane, i.e., Knudsen diffusion.

Figure--6 illustrated a comparison of modified membrane performance with the Robeson curve.³³ Prior to annealing, and after annealing at 190 °C, the PSF membrane demonstrated an H_2/N_2 gas separation performance that exceeded the Robeson upper limit curve. This demonstrated that the membranes

performed well for gas separation, despite the fact that their selectivity was not as great as that of PSF annealed at 120 and 150 °C. However, when annealed at 120 and 150 °C, these PSF membranes demonstrated poor separation performance beneath Robeson curve.

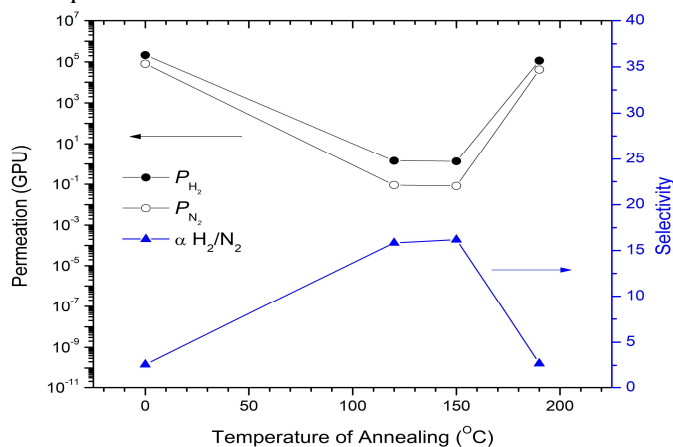


Fig.-5: Single Gasses Permeation and H_2/N_2 Selectivity on the Modified and Unmodified Membranes

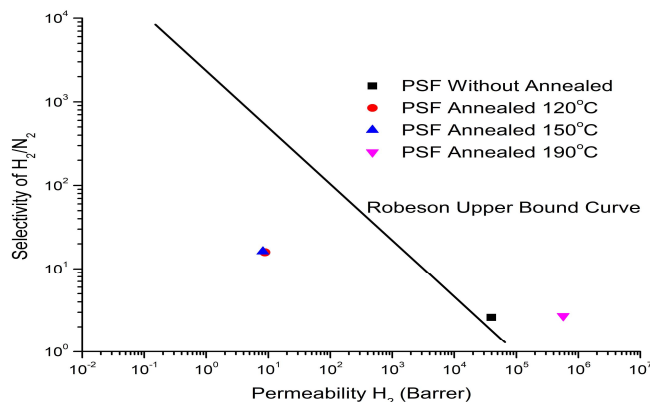


Fig.-6: H_2/N_2 Separation Performances of the Unmodified and Modified PSF Membranes Compared with the Robeson Upper Bound Curve

CONCLUSION

The H_2/N_2 selectivity of PSF membranes effectively increased in this work, and it was discovered that annealing temperature has an effect on the membranes performance by shrinking their pores, as shown by XRD analysis and a drop in the d-spacing. SEM pictures corroborated the XRD data by demonstrating that the annealing treatment caused the polymer matrix in the membrane to become denser. The AFM findings indicated that the PSF membranes prior to annealing had a rougher structure and a greater penetration rate than the annealed PSF membranes. The annealing temperature was changed to establish the optimal conditions for H_2/N_2 gas separation on the PSF membrane. The gas separation performance of the PSF membrane before and after annealing at 190 °C was greater than the 2008 Robeson upper limit curve, indicating that the membranes performed well. Yet, despite their great selectivity, the PSF annealed at 120 and 150 °C performed poorly for gas separation.

ACKNOWLEDGEMENT

The author appreciates the Ministry of Research and Higher Education of Indonesia for providing financial support under the *Penelitian Dasar* research grant, contract number. 1508/PKS/ITS/2022. Moreover, I.S.C. and A.R.W. are grateful for the student exchange scholarship and internship provided by PT PP (persero), PT Pertamina, and Shibaura Institute of Technology, Japan.

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[RJC-6962 / 2021]