CURRENT SCIENCE AND TECHNOLOGY (CST)
VOL. 2, ISSUE 2, 41 – 47
DOI: https://doi.org/10.15282/cst.v2i2.9411

ORIGINAL ARTICLE

Polyvinylidene Fluoride (PVDF) / Poly (Ether Sulfones) (PES) Blend Membrane For CO_2/CH_4 Separation

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ABSTRACT – In this study, a combination of Polyvinylidene fluoride (PVDF) and Poly (ether sulfones) (PES) blend membrane and DMF as solvent component was developed to evaluate the CO_2 and CH_4 separation performance. The gas permeation test was thereafter conducted on the membrane produced. The separation through a membrane works on the theory of permeation based on permeability and selectivity. These two important values were estimated using a set of analytical functions. The membranes produced was then characterized using scanning electron microscopy (SEM) and the Fourier Transform Infrared Spectroscopy (FTIR). The result obtained revealed that a higher permeability for the CO_2 and CH_4 gases when the blending ratio of membrane and solvent of PVDF:PES:DMF/ 5:15:80 were applied. Moreover, the selectivity results showed that the use of the blending ratio of PVDF:PES:DMF/ 20:0:80 produce the highest selectivity (1.3086 GPU) while blending ratio of PVDF:PES:DMF/ 10:10:80 exhibited the least selectivity. In addition, the morphological elucidation revealed the presence of pores for every cross-section composite membrane and this aids the permeability properties of the membrane aggregates at different blending ratio. Also, the FTIR results showed nearly similar functional group characteristics.

ARTICLE HISTORY
Received: 15th Feb 2023
Revised: 01st June 2023
Accepted: 13th June 2023

KEYWORDS
Permeability
Selectivity
Membrane
Gas separation
blending

INTRODUCTION

The demand for an efficient cleaner natural gas has been on an increasing trend in recent times. Methane (CH_4) and Carbon doixide (CO_2) are examples of this natural gas which is the most prevalent component of natural gas and product of fossil fuel combustion[1, 2]. The separations of this important component for the gas streams is of paramount importance in order to obtain efficient energy and prevent the inherent corrosion during the process of transporting the gas. Moreover, the accumulation of this gas portends a great danger to the immediate environment due to the global warming effects [3].

Currently, reducing greenhouse gas emissions is one of the world's most pressing issues. Carbon dioxide (CO_2) is one of the most significant greenhouse gases. More than six and a half billion people use fossil fuels to stay warm, supply energy to light their homes and power industry, and travel using automobiles, buses, boats, trains, and airplanes [4]. Carbon dioxide is produced by the combustion of fossil fuels and released into the atmosphere, which it may contribute to global warming [5].

As a result, CO_2 separation process technology has been developed in response to this issue. Membrane-based technology has witnessed significant development, discoveries, and advancements during the last few decades [6]. This technology's attractive features contain great energy efficiency, ease of design and manufacturing of membrane modules, and environmental compatibility. In this study, the important emphasis was made towards the CO_2/ CH_4 separation, due to its significant and direct importance to the gas industry [7]. Moreover, the market for CO_2 separation is presently dominated by polymeric membranes owing to their comparatively cheap cost of production and processing capability. The transformation of this material into a flat sheet and hollow fibre configurations make them relevant for use. While there have been extraordinarily successful membrane fabrication and development approaches with exceptional performance for each kind of membrane. To enhance the performance of membrane technology, various developments of the polymeric membrane and inorganic membrane especially in gas separation process have been achieved. However, due to the limitation of the polymeric membrane and the high price of the inorganic membrane, membrane became one of the factors in the organic-inorganic hybrid membrane [8].

In practice, the development of adequate membrane material for CO_2 separation proved to be a difficult endeavor. Among the membrane materials, the semi-crystalline Polyvinylidene fluoride (PVDF) gives high purity thermoplastic fluoropolymer. It is among the stiffest and abrasion resistant melt-processible fluoropolymers. It has strong chemical resistance but is susceptible to assault by hot sulfuric acid and hot amines. Moreover, the Poly (ether sulfones) PES have high-performance polymers. The most popular is one made by Union Carbide. PES polymers have high glass transition temperatures. Polymer blending is a valuable strategy for enhancing membrane characteristics. Consequently, membranes are fabricated by physical blending modification, and the effects of polymer ratios on membrane both structure and function are studied. The highly permeable polymer may be employed to fabricate a defect-free selective top layer,

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resulting in a large improvement in membrane selectivity with nearly no loss of permeability[9]. Consequently, the purpose of this study is to build a combination of PVDF and PES blend membrane and to evaluate their CO_2 and CH_4 separation performance. The membranes produced was then characterized using scanning electron microscopy (SEM) and the Fourier Transform Infrared Spectroscopy (FTIR).

EXPERIMENTAL

Materials

In this experiment, Polyvinylidene Fluoride (PVDF) and Poly (ether sulfones) (PES) were utilized as the main materials. PVDF is a thermoplastic fluoropolymer known for its chemical resistance and thermal stability, while PES is a high-performance thermoplastic polymer with excellent mechanical properties and chemical resistance. To prepare the materials for testing, PVDF was melted at a temperature of 177 ºC, and PES was melted at 160 ºC. Dimethylformamide (DMF) was employed as the solvent in this experiment. Then, two types of gases were used for the gas permeation test which are CO_2 and CH_4 gaseous. Both of these gases were internally prepared by the technical staff of the Chemical Engineering Laboratory at the university. The gas permeation test focused on carbon dioxide (CO_2) and methane (CH_4) gases, aiming to evaluate the permeability characteristics of PVDF and PES. This test helps to understand how well the polymers allow the passage of these gases and is relevant for applications such as gas separation, filtration, and membrane technology.

Membrane fabrication

The PVDF and PES were thereafter dried at 60 ºC for 1 hour before the preparation of the dope solution. The wet/dry phase methods were employed in this study for membrane preparation. In this preparation, the membrane cast was allowed to evaporate and then immediately submerged into a non-solvent medium such as water. The membrane product is formed by the phase separation between the solvent (DMF) and non-solvent (water) component, which also assists in the vaporization and polymer clotting processes. Moreover, in the homogenous dope solution preparation of PVDF/PES membrane, the ratio of PVDF:PES:DMF used include 20:0:80, 15:5:80, 10:10:80, and 5:15:80. The mixture was thereafter stirred and dissolved in the solvent. The PVDF/PES mixture was stirred for 3 hours and dissolved in the solvent at 120 ºC. Afterwards, the solution is left for 24 hours to eliminate the trapped gas bubbles.

Furthermore, the membrane was cast using a glass plate. At room temperature, the degassed dope solution was coated with a knife gap of 0.5 mm. The cast film was immediately submerged in a coagulant after 30 seconds of exposure to air. The membrane that had been precipitated was removed from the coagulation bath and washed with running water to eliminate any remaining solvent. At room temperature, the wetting membrane driesin order to form a dry, porous membrane in the form of a flat sheet.

Gas Permeation Test

The membrane was tested for the gas permeation test to determine the permeability and selectivity of the membrane using CO_2 and CH_4. Gas separation through a membrane works on the theory of permeation based on permeability and selectivity. Permeance (P) obtained is used as the basis for estimating selectivity as shown in Equation 1.

$$\frac{P}{l} = \frac{Q}{(A\Delta P)} \tag{1}$$

$$\alpha = \frac{P2}{P1} \tag{2}$$

Where P is the permeability ($cm^3/s.\ cm^2.cm\ Hg$), α is the selectivity, l is the membrane skin layer thickness (cm), Q is the volumetric flow rate (cm^3/s), A is the effective membrane area (cm^2) ΔP is the membrane pressure differential (cm Hg). Equation 2 is the selectivity of membrane to separate the two gasses. The permeability must be changed to in GPU unit with conversion of 1 GPU = 1×10^{-6} $cm^3/s.\ cm^2.cm\ Hg$.

Characterization

Characterization involved the implementation of Fourier Transform Infrared Spectroscopy, FTIR and Scanning Electron Microscopy, and SEM. The SEM device used to examine the membrane morphology [10]. The physical and chemical characterization of the membrane was conducted by using the Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR), respectively. The former was employed to determine the morphological characteristics of the membrane, while the latter determines the functional group characteristics.

RESULT AND DISCUSSION

Effect of blending ratio on the membrane permeability and selectivity

The result obtained shows a higher permeability (0.133 GPU) when the blending ratio of PVDF:PES:DMF/ 5:15:80 were applied. This result indicated that the use of higher solvent during the blending process invariable increases the permeability of CO_2 gas. The same result was obtained for the permeability of CH_4 with the value 1.179 GPU when the blending ratio of PVDF:PES:DMF/ 5:15:80 were applied as shown in Figure 1.

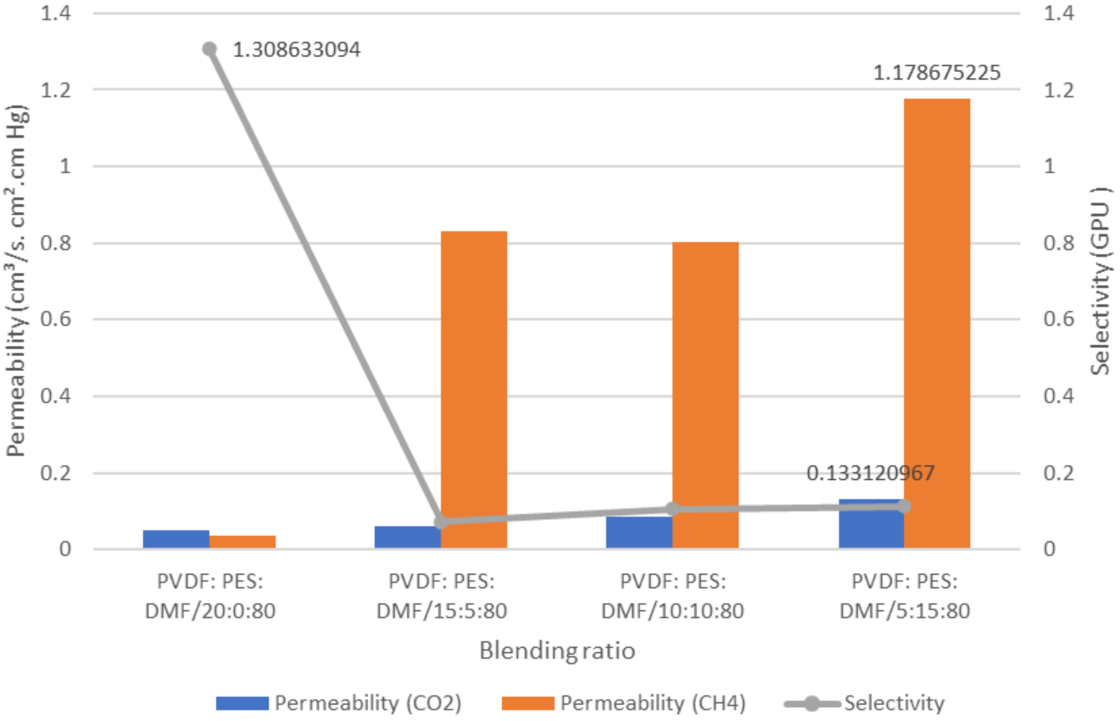


Figure 1. Graphical representation of blending ratio effects on the permeability and selectivity.

From the result obtained as tabulated in Table 1, the order of increasing permeability of methane gas with respect to the blending membranes and solvent ratio (PVDF:PES:DMF) is 20:0:80 > 10:10:80 > 15:5:80 > 5:15:80. However, the order of increasing permeability of CO_2 gas with respect to the blending membranes and solvent ratio (PVDF:PES:DMF) is 20:0:80 > 15:5:80 > 10:10:80 > 5:15:80. This result indicated that the use of higher solvent during the blending process invariable increases the permeability of CO_2 and CH_4 gases [2]. In addition, the degree of selectivity was calculated to determine the performance of the membrane at different blending ratio. The selectivity results showed that the use of the blending ratio of PVDF:PES:DMF/ 20:0:80 produce the highest selectivity while blending ratio of PVDF:PES:DMF/ 10:10:80 exhibited the least selectivity. This indicated that an inverse proportionality between the individual gaseous permeability and the degree of selectivity during the separation process [8].

Table 1. CH_4 Permeability parameters result from the gas permeation tests conducted at different blending ratios

CH_4: Permeability parameters result							
Run	Average Time (s)	V cm^3	Q cm^3 /s	ΔP cmHg	L cm	A cm^2	Permeability cm³/s. cm².cm Hg
PVDF:PES:DMF/ 20:0:80	45.475	50	1.09	75.0062	0.05	19.63	0.0373
PVDF:PES:DMF/ 15:5:80	2.04	50	24.50	75.0062	0.05	19.63	0.832
PVDF:PES:DMF/ 10:10:80	2.1125	50	23.66	75.0062	0.05	19.63	0.803
PVDF:PES:DMF/ 5:15:80	1.44	50	34.72	75.0062	0.05	19.63	1.179

Table 2. CO_2 Permeability parameters result from the gas permeation tests conducted at different blending ratios

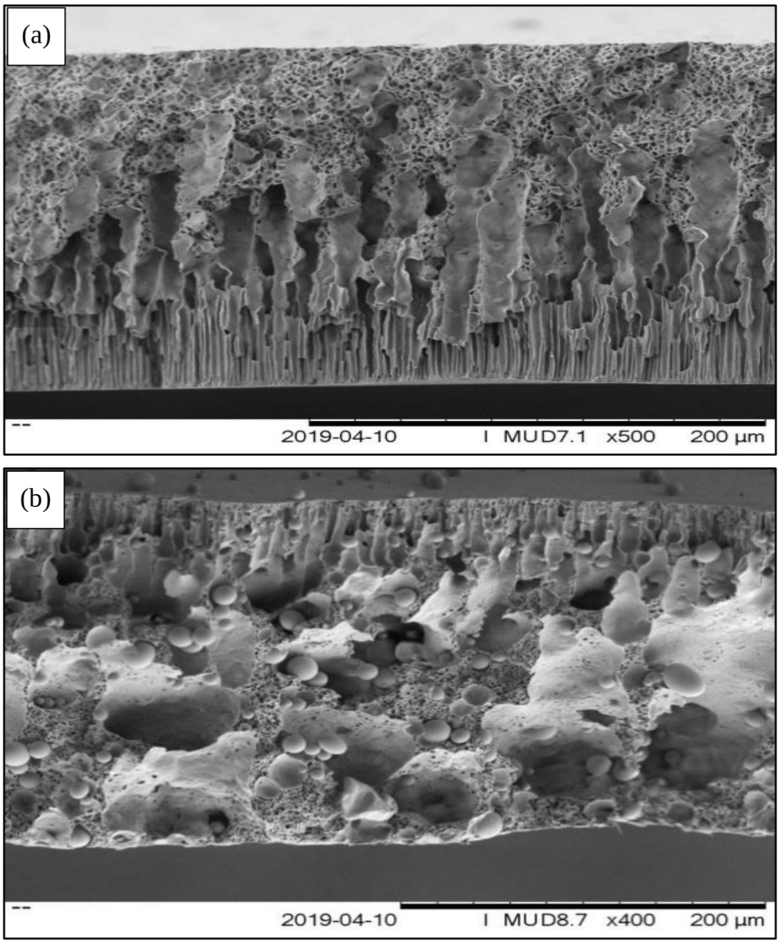
CO_2: Permeability parameters result							
Run	Average Time (s)	V cm^3	Q cm^3/s	ΔP cmHg	L cm	A cm^2	Permeability $cm^3/s.\ cm^2.cm$ Hg
PVDF:PES:DMF/ 20:0:80	34.75	50	1.43	75.0062	0.05	19.63	0.0488
PVDF:PES:DMF/ 15:5:80	28.05	50	1.78	75.0062	0.05	19.63	0.0605
PVDF:PES:DMF/ 10:10:80	19.95	50	2.50	75.0062	0.05	19.63	0.0851
PVDF:PES:DMF/ 5:15:80	12.75	50	3.92	75.0062	0.05	19.63	0.133

Table 3. CO_2/CH_4 Selectivity result from the gas permeation tests conducted at different blending ratios

CO_2/CH_4 Selectivity result (GPU)	
PVDF:PES:DMF/ 20:0:80	1.31
PVDF:PES:DMF/ 15:5:80	0.073
PVDF:PES:DMF/ 10:10:80	0.10
PVDF:PES:DMF/ 5:15:80	0.11

Morphological characterization

The scanning electron microscopy (SEM) was employed to elucidate the cross-sectional and surface morphology of the PVDF and PES membranes. Figure 2(a)-(d) demonstrates the cross-sectional view of the membranes fabricated in this study. Each membranes showed a nearly similar morphology and a dense layer that contributes to their gas permeability. The morphological pattern of the PVDF/PES/DMF blend revealed the blending ratio 20:0:80 shows a less dense structure and this explains the reason for a higher degree of selectivity. This particular blend has been found to have a less dense structure, which could be due to the difference in the chemical structure and molecular weight of the two polymers. PES has a higher molecular weight than PVDF and is more hydrophilic, which could lead to a more open structure when blended with PVDF.



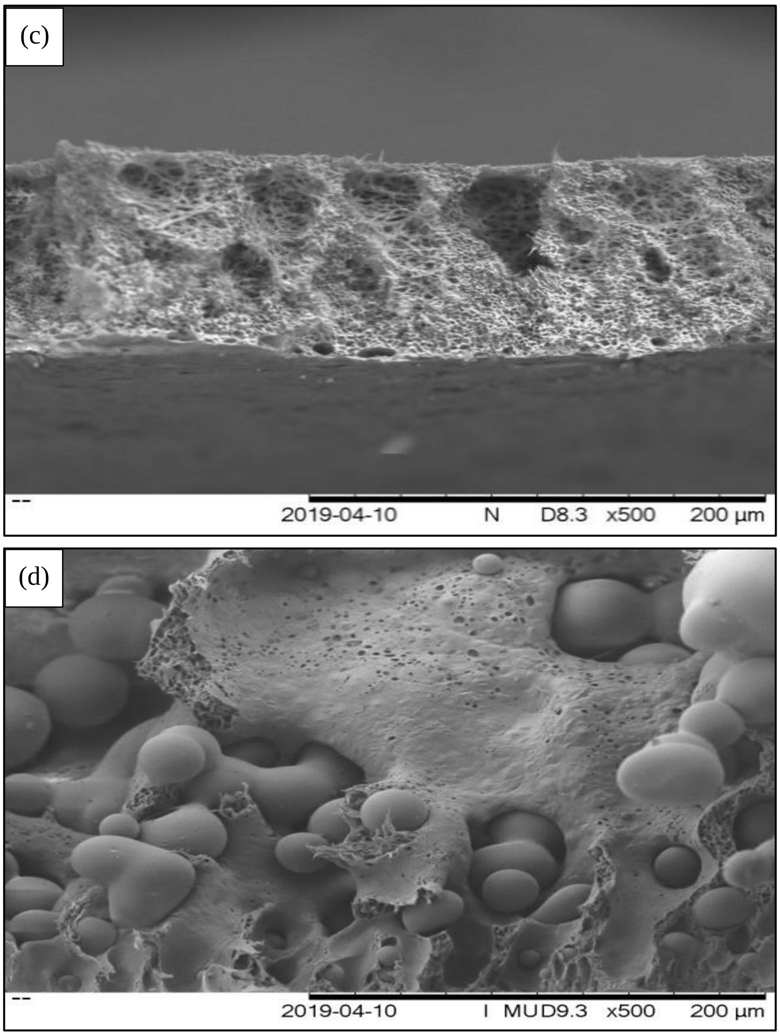


Figure 2. SEM Monograph of PVDF:PES:DMF membrane at ratio (a) 20:0:80 (b) 15:5:80 (c) 10:10:80 (d) 5:15:80.

The less dense structure of the 20:0:80 for PVDF/PES/DMF blend is likely responsible for the higher degree of selectivity observed. Selectivity refers to the ability of a membrane to separate certain molecules or ions from a mixture. A less dense structure can provide more pathways for selective transport, allowing for better separation of target molecules

Moreover, the PVDF/PES/DMF blend in Figure 2(d) for the ratio of 15:5:80 showed larger aggregates which formed a larger pore and this invariably explains the lower performance of the membrane using this blending ratio [2]. During the phase inversion process, the presence of a large amount of PVDF as an additive and a relatively modest amount of PES contributes to the creation of big pores in the membrane matrix [5].

Chemical characterization

Figure 3 shows the spectral wavelength of the composite membrane at different blending ratio. For the entire blending ratio cases, the spectra obtained revealed a sharply defined peak between the wavelengths 750-1000 cm^{-1}. The region of the infrared spectrum between these thresholds is called the fingerprint region. At this region, there are notable large clusters of infrared bands with different vibrations which include the C-O, C-C and C-N single bond stretches, C-H bending vibrations, and some bands due to benzene rings are found in this region. A between 1200-1500 cm^{-1} represents the C-O stretching vibration provides the evidence of cellulosic structure in the membrane [11]. The overall absorption bands from the FTIR analysis confirmed that the PVDF:PES:DMF/5:15:80, PVDF:PES:DMF/15:5:80, and PVDF:PES:DMF/10:10:80 exhibited similar characteristics. However, the membrane structure with the blending ratio, PVDF:PES:DMF/20:0:80 exhibited a different spectra structure which shows the behaviour of the PVDF membrane due to its higher pore structure and this explains their higher degree of selectivity when used in gas separation process.

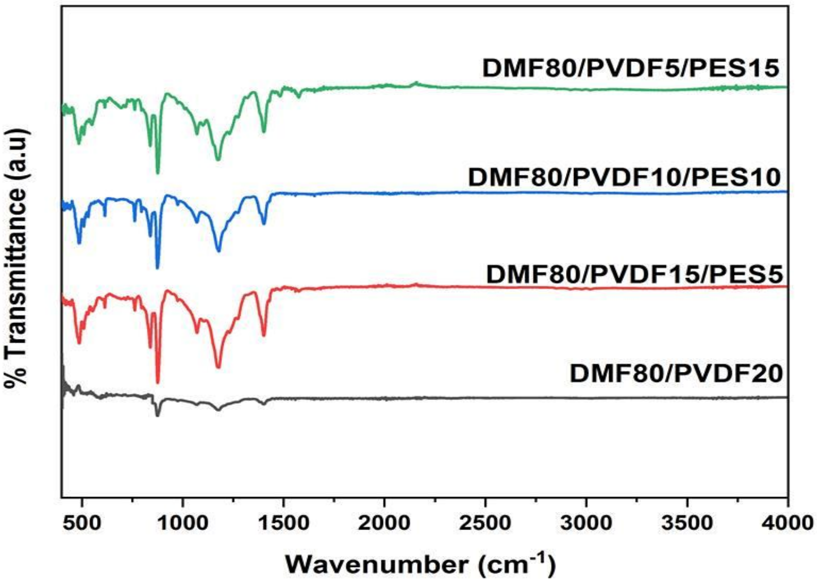


Figure 3. Infrared Spectrum of membranes with the varied blending ratio.

CONCLUSION

The greenhouse gas is one of the world's most pressing challenges, with carbon dioxide CO_2 as one of the primary greenhouse gases. Hence, the development of appropriate membrane material for CO_2 separation has proved to be a difficult challenge. Therefore, the objective of this study is to develop a combination of PVDF and PES blend membrane and evaluate its efficacy in CO_2 and CH_4 separation. The selectivity findings demonstrated that the usage of the blending ratio of PVDF:PES:DMF/20:0:80 produce the highest selectivity while blending ratio of PVDF:PES:DMF/10:10:80 exhibited the least selectivity. This indicated that an inverse proportionality between the individual gaseous permeability and the degree of selectivity during the separation process The morphology analyses of the composite membrane using SEM have been proven the presences of pores on the cross-sectional area of the membrane which explains the permeability and selectivity characteristics of the membrane. Moreover, the result of Fourier Transform Infrared (FTIR) showed the component that contains in the composite membrane showed a sharply defined peak between the wavelengths 750-1000 cm^{-1}, which is regarded as the fingerprint region. On this region notable infrared bands such as C-O, C-C and C-N single bond stretches, C-H bending vibrations, and some bands due to benzene rings were observed. Hence, from the polymer blending for gas separation, the result of SEM and FTIR revealed that the PES polymer does not contribute to the performance of the membrane. However, the PVDF showed an excellent performance membrane with a smaller pore size when compared to the blending structure.

This study shows the effects of the membrane blending structure on the gas separation process. The results obtained shows higher degree of selectivity when using PVDF without blending which implies that the blending of the membrane with other membrane has no significant effects on the performance. Also, due to the effect of microstructural pore size distribution on the selectivity and permeability, the use of other characteristics techniques like Brunauer-Emmett-Teller (BET) technique is essential for the determination of membrane pore size. This will help to further elucidate the on the structure of the membrane and their possible effects on gas separation process

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