



Research Article

Fabrication of polydimethylsiloxane dense layer on polyacrylonitrile composite membrane with varying curing agent ratio

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Abstract

Membrane-based separation is crucial in a variety of sectors. Membrane-based pervaporation is an energy-efficient separation process that is used in the recovery of solvents such as butanol from aqueous solutions. Among the variety of membrane materials, polydimethylsiloxane (PDMS) has shown great promise in pervaporation due to its hydrophobic nature, which favours the selective permeation of organic solvents such as butanol. Nevertheless, standard PDMS membranes typically experience high swelling and compromised structural integrity in organic solvents, which deteriorates their long-term performance. Thus, the purpose of this research is to formulate a composite membrane by adjusting the proportions of PDMS and curing agent in polyacrylonitrile (PAN). The characteristics of the fabricated membrane were investigated using field emission scanning electron microscopy (FESEM), scanning electron microscopy (SEM), contact angle, and swelling index. The 9:2 ratio PDMS/PAN membrane revealed the best characteristics across all characterisations. The surface morphology was outstanding, with a smooth, defect-free selective layer measuring 71.7µm and validated by FESEM and SEM. Additionally, the 9:2 membrane improved crosslinking density and hydrophobicity (128.75° contact angle), reducing swelling by 0.5682 while preserving mechanical flexibility. Butanol separation via pervaporation resulted in a total flux of 4889.24 g/m².h for the 9:2 membrane. This study sheds light on the formulation of PDMS/PAN ceramic membranes with the inclusion of a curing agent, showing their potential for efficient solvent separation in pervaporation systems for industrial applications.

Keywords: ceramic membrane, polydimethylsiloxane, polyacrylonitrile, curing agent, pervaporation

Introduction

In recent years, researchers have focused on n-butanol as a biofuel alternative to bioethanol. Ndaba et al. [1] stated that n-butanol is regarded as the next-generation biofuel since it has several advantages over ethanol, including a larger energy content, less volatility, and a slower rate of moisture absorption. Pervaporation using membranes provides an environmentally friendly and energy-efficient method of recovering butanol. Pervaporation is an advanced membrane-based method for separating azeotropic mixtures or closely boiling solutions. In pervaporation, the selective membrane allows a differential permeation rate dependent on solubility and diffusivity; hence, even such complex liquid mixtures allow the

separation of butanol from water. This process is based on the phenomenon of the preferential permeation of butanol through the membrane resulting from its greater affinity with the membrane material, whereas water molecules interact less favourably with the membrane and hence are less likely to permeate. This selective transportation is facilitated by the concentration gradient and reduced pressure or sweep gas on the permeate side to vaporise the permeated butanol, which is then removed and separated from the water. The benefits of this method include energy efficiency, cost-effectiveness, and environmental friendliness [2]. Researchers generally concentrate on employing hydrophobic pervaporation membranes to recover bio-alcohols (such as ethanol

and butanol) from aqueous solutions. The technology of composite membranes is not particularly new.

A composite membrane frequently has a thin, dense skin layer on a porous organic or inorganic substrate, which improves flux [2]. There are numerous methods for creating composite membranes. Solution-casting, dip-coating, and interfacial polymerisation are the most often used techniques [3]. In dip-coating, the selective layer is applied to the porous support by submerging it in the polymer solution and rising it at a controlled rate, resulting in the creation of the composite membrane. The composite membrane produced via interfacial polymerisation is mainly employed for water filtration. A composite membrane generated via interfacial polymerisation was declared ineffective for gas separation as this procedure produces a hydrogel with decreased cross-linking within the pores of the support. The simplest method for creating a composite membrane is solution-casting, which uses a coating applicator to put the polymer solution onto a porous substrate. It is nearly impossible to prepare membranes with a selective layer of less than 1 mm, as the coating applicator controls the selective layer's thickness [3]. These approaches are intended to create a smooth and dense selective layer for separation purposes. Nonetheless, the membrane's performance can be greatly impacted by the coating technique.

Polyacrylonitrile (PAN) is a popular porous support material in composite membrane fabrication as it has excellent mechanical properties, thermal stability, and compatibility with many coating processes. The support layer's role is to provide the selective layer with a porous and stable structure without hindering its performance. PAN has been proven to remain stable and rigid in various chemical states. As a result, the basic stability of the composite membrane should be maintained. Substrates of PAN support dip-coating and solution-casting to achieve a defect-free selective layer, thus ensuring that the performance of the membrane is consistent and reliable [4]. Apart from that, a favourable pore structure results in thin and uniform polydimethylsiloxane (PDMS) layers, which also enhance the overall flux without sacrificing selectivity. In contrast, PDMS operates as the selective layer due to its hydrophobicity and preferential attraction for butanol molecules, enabling organic-aqueous separation.

The selective layer in a composite membrane serves as the primary barrier that governs the separation process by allowing targeted molecules to permeate while blocking others. Materials such as polyamide (PA) are commonly used as selective layers [5]. However, some of these alternatives suffer from limitations such as low thermal resistance or limited

chemical stability, especially in aggressive or high-temperature environments. Among these materials, PDMS is widely preferred due to its excellent thermal stability, chemical resistance, and mechanical durability. Its hydrophobic nature also makes it particularly effective in separating organic compounds from aqueous mixtures. PDMS-based membranes have demonstrated high permeation flux and selectivity in organic separation processes [6]. Furthermore, traditional PDMS membranes frequently exhibit brittleness and poor durability due to their lack of mechanical strength. These constraints can result in deformation or failure over extended operation or under high-pressure settings, significantly lowering flux and selectivity over time. Thus, compared to PA-based membranes, the PDMS–PAN combination offers great organic selectivity and structural resilience. The development of composite membranes that incorporate curing agents into PDMS with more mechanically robust substrates, including PAN, is crucial for resolving these problems. This technique aims to generate a smooth, dense, and defect-free membrane surface, which improves separation performance and provides long-term operating stability in demanding situations.

Extensive research has been conducted to overcome these limitations, aiming at modifying the physical, chemical, and mechanical properties of PDMS membranes. Among these, one approach was the use of composite materials, which are a combination of PDMS with other materials such as polymers, zeolites, and nanomaterials to enhance their performance [7]. The addition of materials such as polysulfide, polyvinylidene fluoride, and graphene oxide into PDMS has been used to enhance the mechanical strength, chemical stability, and permeability of the membranes. These composite materials are expected to enhance the overall performance of the PDMS membranes by optimising the balance between selectivity and flux. These modifications significantly enhance the butanol recovery rate while minimising energy consumption.

A crosslinker, often referred to as a curing agent, is a chemical that is added to a base polymer, such as PDMS, to initiate the crosslinking process. According to Bardelli et al. [8], commercial PDMSs are commonly supplied in two liquid-component kits, including the elastomer base and curing agent. Sylgard184 is one of the most regularly used PDMS formulations. The curing agent forms a three-dimensional network that stabilises and hardens the polymer structure. The physical and chemical characteristics of membranes, including their flexibility, mechanical strength, and surface morphology, as well as their separation ability, are directly impacted by crosslinking. Although it may

reduce flexibility and permeability, an increase in the concentration of the curing agent will often result in a higher crosslink density and a more rigid and thermally stable membrane. On the other hand, a decrease in crosslink density may result in a reduction in mechanical strength but an increase in permeability. As a result, one crucial factor in membrane preparation is the curing agent ratio. The most widely used formulation is the 10:1 base-to-curing agent ratio, as it provides an optimal balance between mechanical stability and flexibility. This ratio has been extensively adopted in membrane research due to its reproducible curing properties and suitable material characteristics. In this study, the 10:1 ratio was employed following the experimental validation by [9]. Some earlier research has demonstrated that changing the ratio of the curing agent can significantly improve membrane performance [9]. Although earlier research has looked at various membrane modifications, there has been little exploration into the effect of varied PDMS-to-curing agent (Sylgard 184) ratios on PAN-supported structure in terms of membrane morphology, crosslinking density, and pervaporation efficacy. To fill this gap, this study attempts to elucidate the characteristics of PDMS dense-layer manufacturing on PAN composite membranes with different PDMS and curing agent ratios (10:1, 9:2, and 8:3). The results offer a scalable method for developing membranes for effective butanol recovery in industrial separation processes, as well as fresh insights into how curing chemistry might optimise membrane performance.

Materials and Methods

Chemicals and instrumentation

Dimethylformamide (DMF, 99.9% pure), polyacrylonitrile (PAN), polydimethylsiloxane (PDMS), Sylgard 184 (silicone elastomer base and curing agent), and n-butanol were used in this study. All chemical reagents were of analytical grade and were used as received. The membranes were assessed using Fourier-transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FESEM), scanning electron microscopy (SEM), atomic force microscopy (AFM), contact angle goniometer, and tensile strength tester. The swelling index was also determined as part of the characterisation.

Preparation of PDMS/PAN membrane

DMF, PAN, PDMS, and Sylgard 184 were employed to formulate the PDMS/PAN membrane. The samples were produced using PDMS Sylgard 184, which consists of a mixture of the base material (silicon elastomer) with its curing agent (crosslinker). Prior to membrane characterisation, PDMS/PAN were produced using the procedure adapted from previous

research by Knozowska et al. [10]. PAN and DMF (99.9% pure) were heated and agitated until they dissolved entirely. To maintain consistent support thickness across samples, the PAN solution was poured onto the petri dish with the same diameter (90mm) and set solution volume (20 mL). The samples were then dried in the oven at 50°C for approximately 24 hours. The dry and solidified PAN support layer was covered with the PDMS Sylgard 184-based curing agent. The base-to-curing agent ratios (10:1, 9:2, and 8:3 w/w) were prepared by weighing each component and mixing thoroughly before coating. The mixture was stirred thoroughly for 5 minutes and subsequently dried for about 2 hours at 90°C. The same procedure was carried out for ratios of 9:2 and 8:3. The selection of the experimental range for the variables is in line with earlier research by Kim et al. [11]. After that, the dried membrane was removed from the petri dish and kept at room temperature in a ziplock bag. The procedures for preparing and characterising the PDMS/PAN membrane are depicted in **Figure 1(a)**.

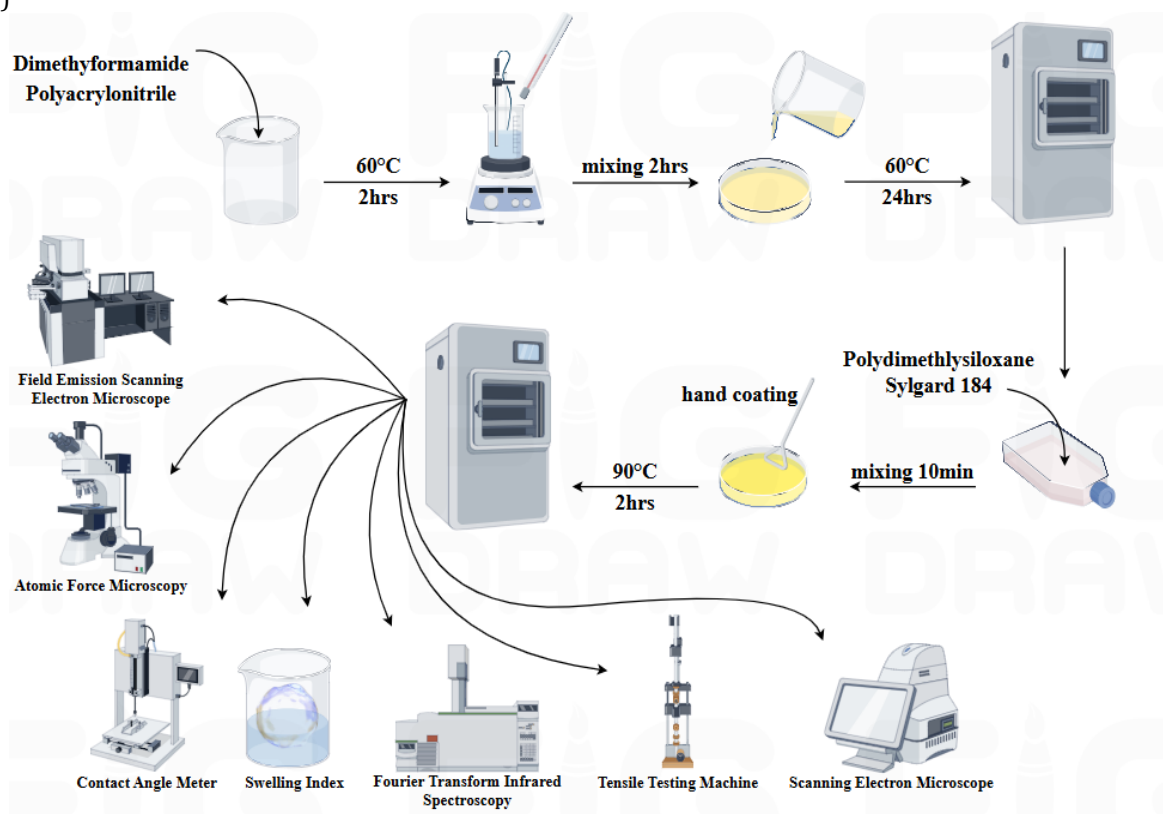
Pervaporation testing

The performance of the best fabricated PDMS/PAN membrane with optimal morphology, hydrophobicity, and swelling resistance was assessed using the pervaporation process, as shown in **Figure 1(b)**. Pervaporation processes were carried out at 45°C with membrane area (A) of 0.007854 m², feed concentration of 100% n-butanol, and permeation time (t) of 15 minutes at 0.04 MPa vacuum pressure. The liquid n-butanol was first stored in the feed tank and then continually circulated through the system by means of peristaltic pump. The feed passed through membrane cells containing selective PDMS/PAN membrane, which allows the desired components to permeate while retaining others. The pressure on the permeate side was reduced by vacuum pump to enhance the vaporisation of selected components during their diffused path across the membrane. The vaporised permeate was then condensed and collected in the glass collector, while the components that could not permeate remained in the feed stream. The permeate in vapour form was collected on the downstream side with cold trap or condenser. The permeate was collected and carefully weighed with a balance over a specified period. Finally, the flux was computed using Equation (1):

$$J = \frac{m}{(A \times t)} \quad (1)$$

where J is the permeate flux (kg / m²· h), m is the mass of permeate collected (kg or g), A is the effective membrane area (m²), and t is the permeation duration (h).

a)



b)

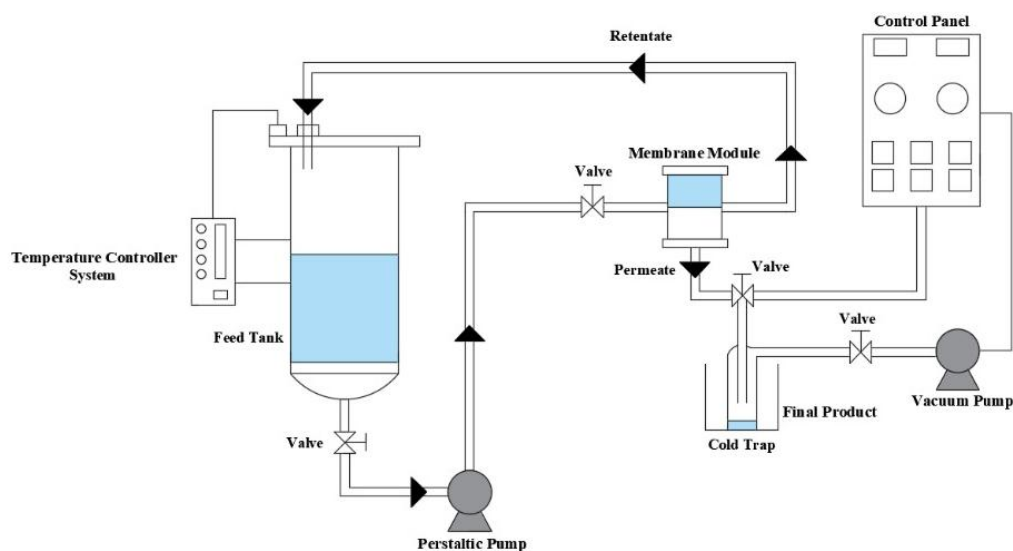


Figure 1. Schematic diagrams of (a) membrane fabrication steps and (b) pervaporation process setup

Membrane characterisation

The ability of PDMS/PAN membranes to withstand stretching pressures is indicated by their tensile strength. According to ASTM D412 guidelines, motorised testing apparatus was used to perform tensile testing on the PDMS/PAN membrane samples

at room temperature [9]. Specimens were moulded into dumbbell shapes both parallel and perpendicular to the magnetic field. The testing apparatus continued to expand the samples at a steady rate of 30 mm/min until failure occurred. The tensile strength was calculated by dividing the sample's cross-sectional

area by the greatest force absorbed before breaking. This technique provides information about the material's mechanical strength and flexibility. Young's modulus assessed the durability of the PDMS/PAN membrane, demonstrating its capacity to withstand deformation under stress. The strength and flexibility of PDMS were balanced at the typical 10:1 (w/w) ratio. However, changing the concentration of the curing agent can affect the modulus [9]. Universal testing machine was used to conduct the tensile test on the PDMS/PAN membrane by stretching the sample at a consistent rate to determine the membrane's Young's modulus. After plotting the stress-strain curve, the linear portion of the curve was used to calculate Young's modulus using Equation (2):

$$E = \frac{\frac{F}{A}}{\frac{\Delta L}{L_0}} \quad (2)$$

where E represents Young's modulus, F represents force (N), A represents cross-sectional area, ΔL represents elongation, and L_0 represents the membrane's original length.

The elongation at break test was conducted on materials by stretching the material sample at a constant rate until it broke. First, the sample was prepared and then mounted into the testing machine fitted with grips to hold the material in place. While the material was being stretched, the machine recorded the force and elongation. Elongation at break was calculated as the percentage increase in length from the original sample length before rupture. It examined the material's flexibility, toughness, and tensile properties. This experiment followed ASTM D412 standards with slight modifications [12].

The swelling index for the developed PDMS composite membranes was evaluated through swelling experiments in which membrane samples were soaked in distilled water for 5 minutes under atmospheric conditions. The degree of swelling was defined as the water uptake after 5 minutes and was calculated using Equation (3):

$$\text{Degree of swelling (\%)} = \frac{W_2 - W_1}{W_1} \times 100\% \quad (3)$$

where W_1 is the weight of the dry membrane and W_2 is the weight of the swollen membrane.

Fourier-transform infrared spectroscopy (FTIR) was employed to identify functional groups and verify the polymer structure of the PDMS/PAN membrane. Solid membrane samples were placed in the Agilent Cary 360 FTIR spectrometer, where an infrared beam was transmitted through the material. The absorbance spectrum was measured from 4000 to 400 cm^{-1} .

The PDMS/PAN membrane's cross section was investigated using scanning electron microscopy (SEM; EM-30AX Plus). After being frozen in liquid nitrogen, the membrane was fractured to create a vertical cut. Before imaging, the samples were covered with a thin conductive layer, such as gold, to prevent charging. SEM enabled detailed evaluation of pore size, distribution, and structure, as well as internal characteristics crucial for processes such as gas separation and filtration. Field emission scanning electron microscopy (FESEM; JEOL-JSM-7600F) was used to examine the surface morphology of the PDMS/PAN membrane.

Atomic force microscopy (AFM), using NanoScope software (Version 1.8) and scanning probe microscope (Bruker Corp.), was employed to evaluate the topography and roughness of the membranes. The membrane samples were placed on the glass specimen holder measuring about 1 cm $\times$ 1 cm. The tapping mode (5 $\times$ 5 μm scanning area) was used to scan the samples at two locations in air.

The hydrophilicity of the membrane surface was evaluated using the contact angle measurement approach (VCA Optima Products Inc), which used the static sessile drop method to determine the degree of wetting between water and the membrane surface. The average contact angle from three random sites was measured to minimise experimental errors.

Results and Discussion

Characterisation of PDMS/PAN based membrane

Figure 2 shows the FTIR spectra of pure PAN and the PDMS/PAN membranes. PAN's spectra showed a peak at 2240 cm^{-1} , indicating the $\text{C}\equiv\text{N}$ stretching vibration of the nitrile group, a unique feature of the compound [13]. A smaller peak around 1450 cm^{-1} was attributed to CH_2 bending modes, whereas other peaks in the 2850–3000 cm^{-1} range were ascribed to C–H stretching vibrations from aliphatic CH_2 groups [14]. The $\text{C}\equiv\text{N}$ peak at about 2240 cm^{-1} in the PDMS/PAN membranes verified that the structure of PAN was preserved. Asymmetric stretching of PDMS/PAN membranes by Si–O–Si was identified as the cause of the new absorption bands that appeared at 1000–1100 cm^{-1} and 1260 cm^{-1} . The presence of both polymers was demonstrated by the overlapping contributions from C–H stretches in the region near 2900 cm^{-1} in both PAN and PDMS/PAN membranes. These results indicated that PAN and PDMS/PAN membranes formed primarily a physical blend rather than a chemical connection as there were no notable peak shifts in the $\text{C}\equiv\text{N}$ stretch [15].

Liu et al. [16] found an absorption peak at 1257 cm^{-1} attributed to Si–CH₃ in pure PDMS membrane, which is consistent with the results of this study. According

to these findings, the PDMS/PAN membranes maintain the fundamental properties of both polymers, making them appropriate for uses requiring both the flexibility of PDMS and the structural stability of PAN. The successful incorporation of PDMS into PAN was confirmed by the FTIR analysis, which showed a physical mixing rather than chemical bonding. This composite structure may be useful in applications where the distinct features of both polymers are desired. To improve interfacial interactions and the overall performance of the material, future research should investigate processing modifications.

The surface morphology of PDMS/PAN membranes prepared with varying base-to-curing agent ratios (10:1, 9:2, and 8:3) is displayed in Figure 3. Figure 3(a-c) shows the surface membrane morphology identified using FESEM. Variations in the curing agent ratio caused substantial changes in the membrane surface. The membrane prepared at 8:3 ratio (**Figure 3(a)**) exhibited micro-sized gaps and possible surface flaws, as well as rough and uneven surface. These characteristics may be related to excessive crosslinking, which causes excessive stiffness, shrinkage, and stress cracking during the

curing process of the membrane [17]. Excessive usage of the curing agent might result in altered network formation, which makes the structure less compact and brittle. The 8:3 membrane's surface roughness and flaws could have a detrimental effect on its mechanical durability and selective performance, since too much crosslinking can cause distortions and decrease flexibility. On the other hand, the membrane prepared at 9:2 ratio (**Figure 3(b)**) has a slightly rougher surface than the 10:1 sample. Higher levels of crosslinking in the PDMS matrix may cause local stiffness and potential microphase separation, which could account for the rough shape [11].

This condition may marginally impact the homogeneity of the membrane's surface. **Figure 3(c)** illustrates the smooth and dense structure of the membrane's surface at 10:1 ratio, with few visible flaws. One possible explanation for this homogeneous surface is an ideal crosslinking reaction that permits the formation of a well-structured polymer network [18]. The lack of pores or fractures indicates that the membrane is stable and has high integrity, making it appropriate for pervaporation performance. Thus, among the three formulations, the 10:1 and 9:2 formulations seem to be the most advantageous.

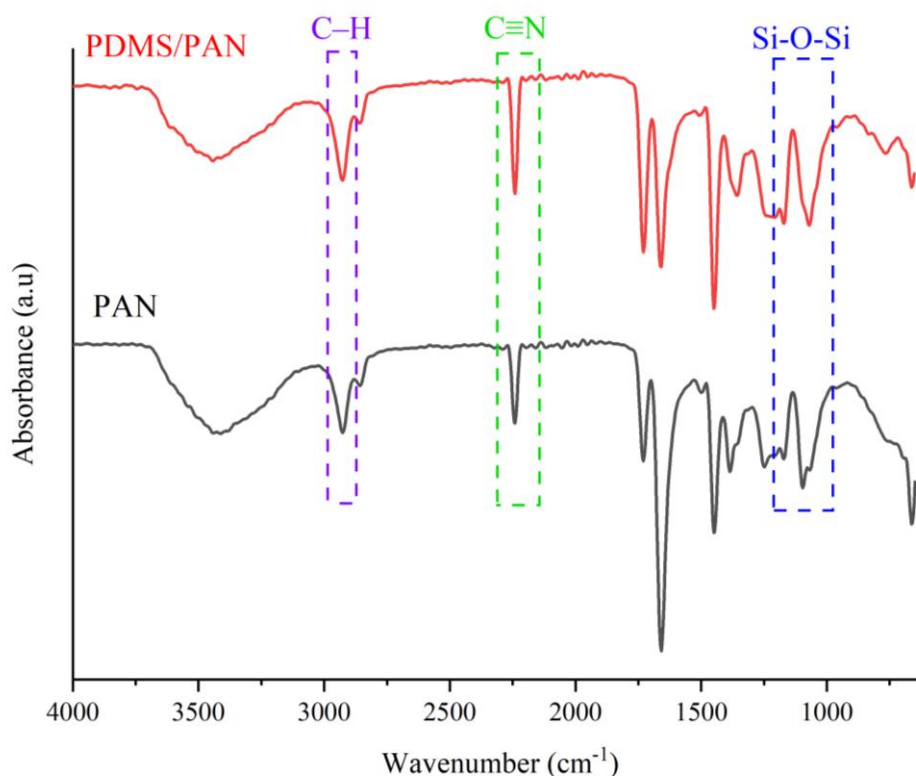


Figure 2. FTIR of PAN and PDMS/PAN-based Membranes

Typical SEM images of the cross-section of PDMS composite membranes supported on the flat-sheet PAN support layer with varying PDMS layer thicknesses are shown in **Figures 3(d), (e), and (f)**. **Figure 3(d)** illustrates that the membrane with 10:1 ratio had thickness of 114.9 μm . In contrast, the membrane prepared with 9:2 ratio exhibited PDMS layer thickness of 71.7 μm (**Figure 3(e)**). Among the three ratios, the 8:3 membrane had the greatest PDMS thickness, measuring 131 μm (**Figure 3(f)**). This behaviour may be influenced by coating time, acceleration, and speed [11]. Since hand coating was applied, the main PDMS layer thickness may also be

affected by the curing agent ratio. Furthermore, the thickness of the PDMS layer on the PDMS/PAN membrane may be influenced by both the volume applied during coating and the viscosity of the PDMS solution. The results indicated that the thickest PDMS layer was found in the 8:3 sample, as the additional curing agent caused the membrane to solidify more quickly and retain more PDMS. Even though the 9:2 PDMS layer was the thinnest, the balanced curing process created a softer and smoother membrane. According to Zhu et al. [18], the thinnest membrane is preferable, as it may result in higher permeate flux during the pervaporation process.

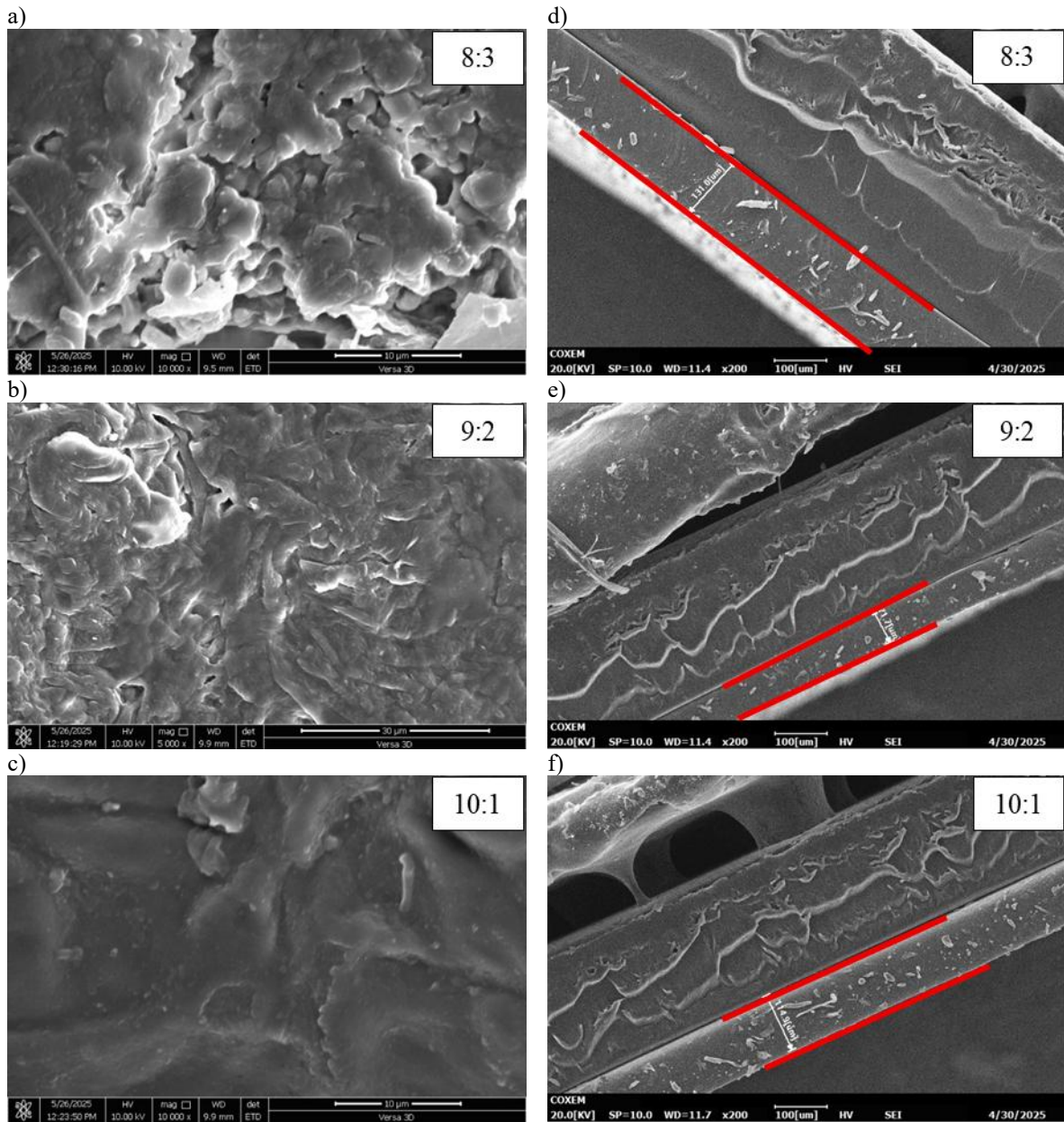


Figure 3. Surface morphologies (a-c) obtained using FESEM and cross-sectional views (d-f) of PDMS/PAN membranes using FESEM and SEM, respectively

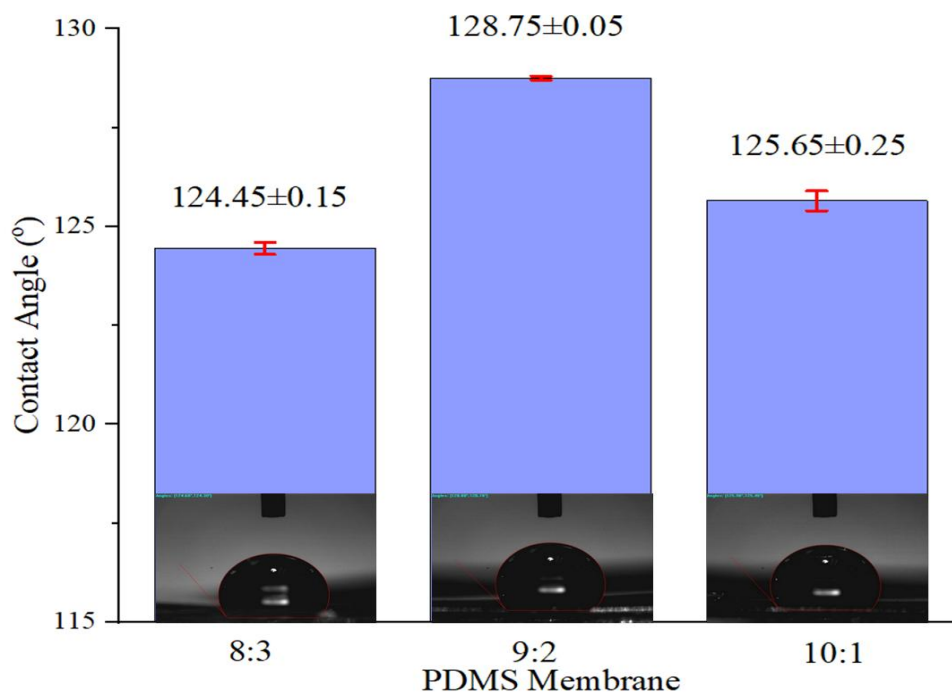


Figure 4. Static contact angle on the surface of PDMS/PAN membranes with 8:3, 9:2, and 10:1 ratio

Another crucial element influencing membrane fouling performance in the pervaporation process is the hydrophilicity and hydrophobicity of the membrane surface. The contact angle is primarily used to describe these properties, as it reflects the degree of water affinity on the wet membrane surface, measured using the static sessile drop method. Higher membrane surface hydrophilicity is generally indicated by a smaller contact angle. Conversely, a higher contact angle value indicates that the membrane surface is more hydrophobic. Figure 4 illustrates the contact angle analysis used to evaluate the surface hydrophobicity of PDMS/PAN membranes by depositing water droplet on the membrane surface. The water contact angle did not vary significantly across the different PDMS/PAN membrane ratios. In Figure 4, it demonstrated that the 8:3 base polymer-to-curing agent ratio exhibited the lowest contact angle of 124.45° among other samples, indicating low hydrophobicity. In contrast, the 9:2 membrane showed the highest contact angle of 128.75°, suggesting enhanced hydrophobicity. One possible explanation is the high crosslinking density within the PDMS network, which may prevent water penetration through the membrane. This limited water permeability further reflects the membrane's high selectivity. Overall, the results demonstrated that the appropriate ratio of Sylgard 184 curing agent to base polymer enables the formation of crosslinked PDMS/PAN membrane with desirable hydrophobic surfaces. The fabricated membranes are suitable for

efficient solvent separation during the pervaporation process [18].

Venkatachalam and Hourlier [19] proposed that crosslinking between PDMS and Sylgard 184 curing agent occurs via platinum-catalysed hydrosilylation reaction. Previous studies have employed DSC and other thermal techniques to analyse the heat of reaction to propose potential mechanism of PDMS crosslinking [11]. However, due to the requirement for extensive heat research, direct validation of this crosslinking mechanism was not feasible in this study. To statistically validate the crosslinking behaviour and to correlate curing kinetics with the observed changes in mechanical and separation performance, such thermal analyses will be included in future studies.

AFM analysis was carried out to investigate how different membrane formulations affected antifouling qualities by examining surface roughness. The PDMS surface roughness was evaluated using AFM, as shown in **Figure 5**. As depicted in **Figure 5(a)**, the 8:3 membranes showed wider valleys and coarser peaks compared with the 9:2 membranes. This was confirmed by the AFM image, with R_q (3.126 nm) and R_a (6.658 nm) values revealing higher surface roughness for the 8:3 membranes. In contrast, the 9:2 membranes (**Figure 5(b)**) displayed a notably smoother surface, with R_a of 3.297 nm and R_q of 4.716 nm, suggesting a more uniform and compact structure

attributable to greater crosslinking density. This ratio appeared to offer the best balance between flexibility and structural integrity, yielding a more uniform membrane surface. These findings suggest that PDMS chains are enriched at the membrane surface due to phase separation caused by thermodynamic incompatibility between PDMS and PAN [11, 20].

AFM analysis further demonstrated that the optimized crosslinking density in the 9:2 PDMS/PAN membrane reduced surface roughness, thereby lowering the likelihood of fouling. These findings corroborate the morphological improvements observed in FESEM analysis. The 10:1 PDMS/PAN membrane had the highest surface roughness ($R_q = 8.648$ nm), much greater than that of the 9:2 (4.716 nm) and 8:3 (6.658 nm) membranes. According to Cabrera et al. [21], quantitative roughness assessments are based on the arithmetic average of surface heights, defined by the R_a parameter. The increased roughness of the 10:1 membrane could result from insufficient crosslinking, which created loosely packed polymer networks with

greater surface mobility and heterogeneity, leading to rougher and uneven surface. Consequently, the rougher surface of 10:1 membrane may promote fouling and reduce permeate flux, as more molecules are likely to accumulate in surface valleys and deposited onto the membrane.

Tensile strength

In general, increasing the curing agent content (from 10:1 to 8:3) caused an increase in membrane stiffness, as reflected by higher Young's modulus. The stress-strain curve, as shown in **Figure 6(a)**, indicated that the 8:3 sample had the highest stress value, corresponding to higher curing agent content compared with the other samples. This observation is verified by the results in **Figure 6(b)**, where the 8:3 ratio displayed the greatest Young's modulus, followed by 10:1, and the lowest value was observed for 9:2. The increase in curing agent concentration enhances crosslinking within the PDMS structure, thereby enhancing membrane rigidity and tensile strength [22].

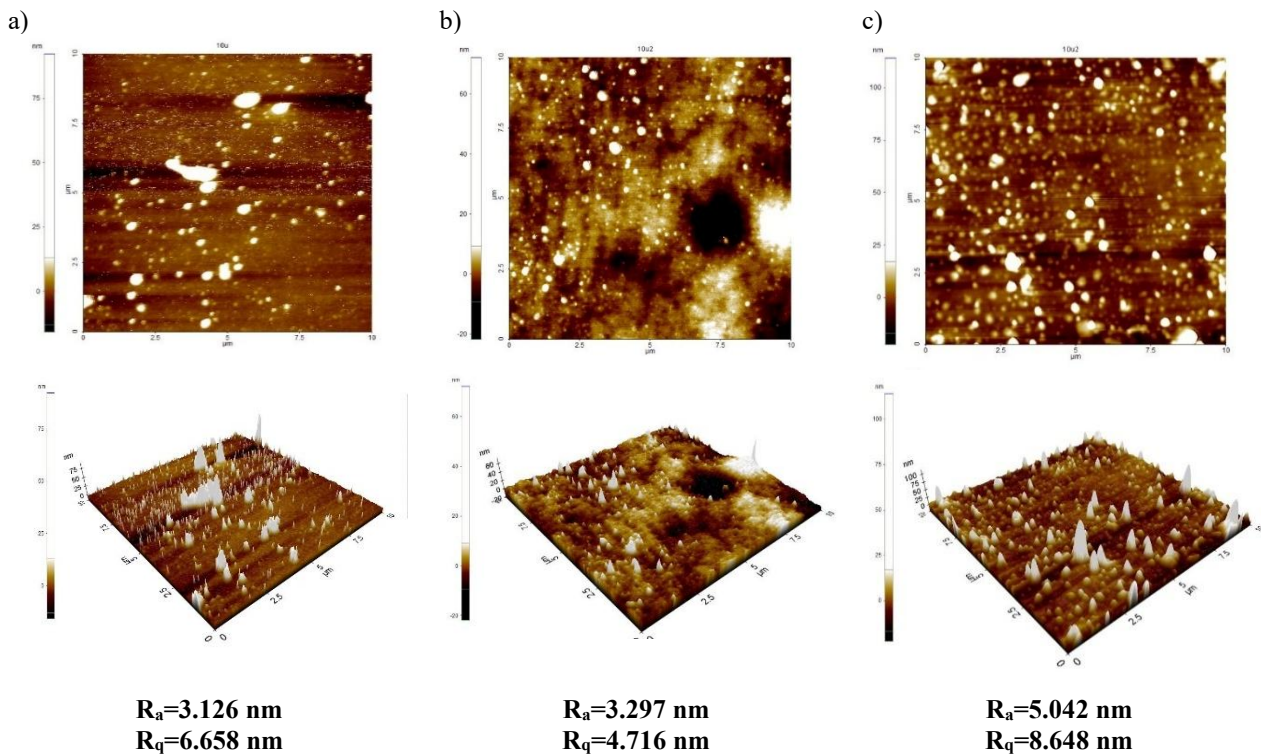


Figure 5. AFM surface roughness images with average roughness (R_a) and root-mean-squared roughness (R_q) for PDMS/PAN membranes: (a) 8:3, (b) 9:2, and (c) 10:1

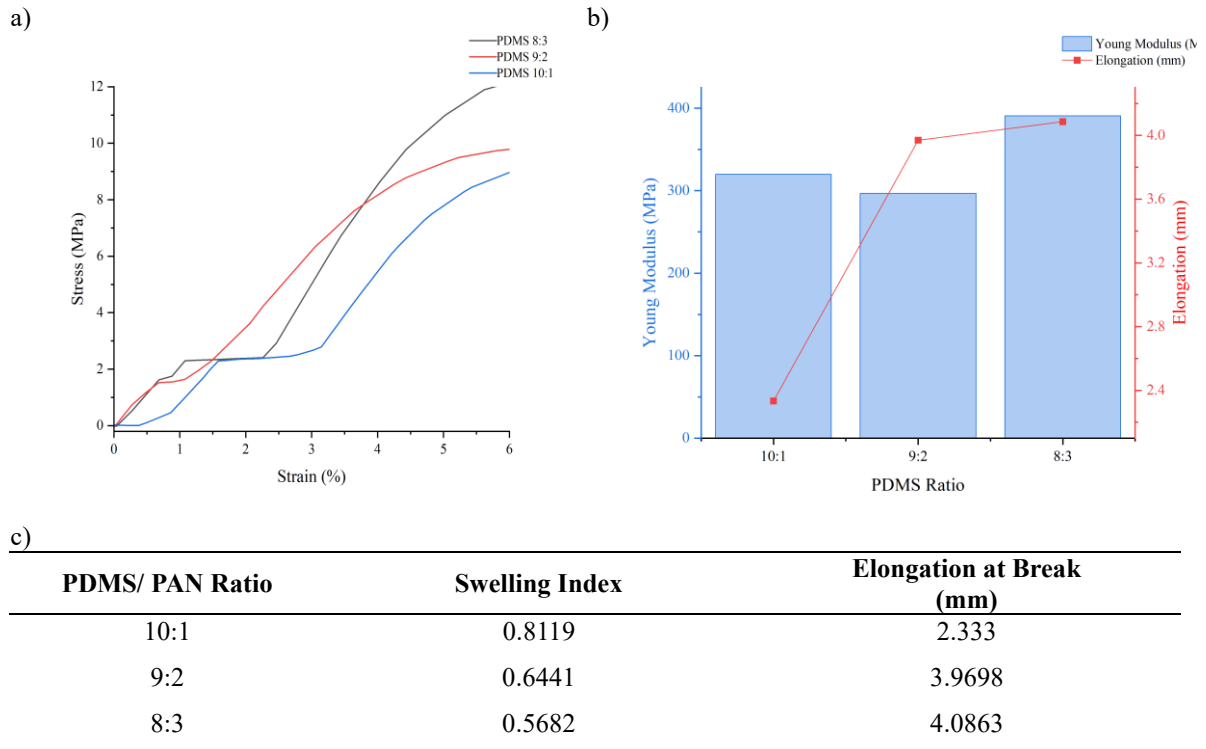


Figure 6. Tensile strength of PDMS/PAN membranes

However, increasing stiffness also affected elongation at break. As depicted in **Figure 6(b)**, elongation increased with higher curing agent content, although the trend was not perfectly linear. This behaviour may be due to the balance between flexibility and brittleness of the membrane. For instance, the 8:3 membrane exhibited greater flexibility than the other samples, possibly due to a lower crosslink density that allowed more polymer chain mobility before fracture. In contrast, the 9:2 membrane exhibited significant elongation at break, indicating that a modest curing ratio resulted in a more balanced network structure. These findings imply that mechanical behaviour is influenced not only by the amount of curing agent used, but also by how crosslinking density affects the balance of stiffness and flexibility. As a result, the 9:2 ratio offers the best balance of strength and elasticity, making it ideal for pervaporation applications requiring both mechanical stability and flexibility.

Generally, the maximum mechanical strength and stiffness were observed for the 8:3 PDMS ratio, making it suitable for applications where structural stiffness is critical. On the other hand, the 9:2 ratio exhibited a well-balanced mechanical behaviour, combining sufficient strength with enhanced flexibility. Such variability in mechanical properties is of vital concern when choosing a membrane formulation for specific applications, such as

separation or filtration processes, where both strength and elasticity are required.

The swelling index and elongation at break of each membrane are shown in **Figure 6(c)**. The 10:1 PDMS ratio exhibited the highest swelling index (0.8119), attributed to its lower curing agent content, resulting in significantly low crosslinking density within the PDMS network. A loosely PDMS network allowed more solvent molecules to penetrate the membrane. In contrast, the 8:3 PDMS ratio, with the highest curing agent content, showed a comparatively low swelling index of 0.5682. This notable decrease in swelling indicates highly crosslinked polymer network, which significantly reduces the amount of free volume for solvent penetration. In addition to limiting polymer expansion, such dense structures improve its mechanical stability and chemical resistance. Based on morphological, mechanical, and surface property evaluations, the PDMS/PAN membrane prepared at 9:2 base-to-curing agent ratio was chosen for pervaporation testing, as it demonstrated the most favorable balance of hydrophobicity, crosslinking density, and structural integrity.

Comparison with previous studies on PDMS-based membranes in pervaporation

The separation performance of the PDMS-based membranes developed in this study was compared with that of various composite membrane reported in

Table 1. Comparison of butanol flux with previous studies on various PDMS-based membranes

Membrane	Types of gas	Flux ($\frac{g}{m^2.h}$)	Finding	References
9:2 PDMS/PAN	Butanol	4889.24	The PDMS/PAN membrane exhibited a smooth, dense, and permeable structure with low selectivity but high flux when operated at 45 °C.	This study
TAO/ZIF-8/K-PDMS	Butanol	2890	ZIF-8 metal and PDMS with silane create a more stable multilayer composite membrane by in-situ transformation.	[25]
Fluorinated PDMS	Butanol	360	The hydroxyterminated of PDMS and flourosilane undergo a crosslinking process to produce a hydrophobic PDMS membrane. The fluorinated PDMS membrane demonstrated steady separation performance and outstanding anti-biofouling properties.	[26]
P-ZIF-L@PDA/PDMS	Butanol	508.70	Selecting highly reactive silane coupling agents for surface modification improves the performance of mixed matrix membranes.	[27]

earlier research (Table 1). Previous studies have shown that PDMS-coated membranes exhibit significantly enhanced butanol permeability [23][24]. Surface modification of composite membranes with PDMS has demonstrated outstanding separation performance due to the well-dispersed nature of PDMS. This enables efficient adjustment of solvent transport characteristics through both diffusion and adsorption mechanisms. The PDMS/PAN membrane with 9:2 base-to-curing agent ratio indicated the highest flux. This was due to its balanced network structure, which was neither too dense nor too loose. At this ratio, the crosslinking degree was optimised, where the membrane allowed butanol molecules to permeate effectively while maintaining adequate membrane strength. The curing agent concentration sets the interchain distance. Insufficient curing results in a loosely crosslinking network with poor selectivity, while excessive curing results in a dense network that suppresses permeability. Therefore, the 9:2 ratio represents optimal formulation, providing effective butanol separation.

Conclusions

A high-performance PDMS/PAN membrane was successfully fabricated, with the 9:2 ratio membrane demonstrating the most stable among the three formulations tested. The 9:2 membrane was selected for pervaporation to separate butanol, achieving a total flux of 4889.24 g/m² h. The selection was further supported by SEM and FESEM analyses, confirming that the 9:2 membrane was the thinnest of the three. Although its surface was slightly rougher, this morphology was acceptable and likely contributed to greater permeate flux during the pervaporation. In terms of mechanical performance, the 9:2 PDMS ratio provided a superior balance between strength and flexibility compared with the 10:1 and 8:3 ratios. While not the strongest or stiffest membrane, it offered sufficient mechanical strength combined with high degree of flexibility. This makes it particularly appropriate for separation and filtration applications that demand both durability and elasticity. The balanced performance of the 9:2 ratio membrane makes it more practical and adaptable for solvent

separation. Its high crosslinking density contributed to excellent hydrophobicity, with contact angle of 128.75°, preventing water penetration and improving selectivity. The 9:2 membrane also exhibited lower swelling index than the 10:1 ratio, further confirming stronger crosslinking. This dense network structure enhances mechanical stability and chemical resistance while minimising swelling and reducing solvent penetration during pervaporation. In conclusion, beyond the PDMS-to-curing agent ratio, the coating method may also influence membrane performance. Optimizing the coating technique could further improve membrane selectivity and overall properties for pervaporation applications. Future work will involve systematic pervaporation testing of all curing ratios to validate and compare flux–selectivity trade-offs across formulations.

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