Research Paper

Polyvinylidene Difluoride-co-Polyethylene Glycol Membrane for Biohydrogen Purification from Palm Oil Mill Effluent Fermentation

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Highlights

- PVDF membrane fabricated at different C_p to separate H_2 fermented gases.
- Highest H_2 permeability, selectivity and purity were obtained using C_p =18wt%.
- Surface modification of membrane further enhanced the selectivity.
- Modified PVDF/PEG membrane reached 96% H_2 purity compared to control (85%).

Graphical abstract
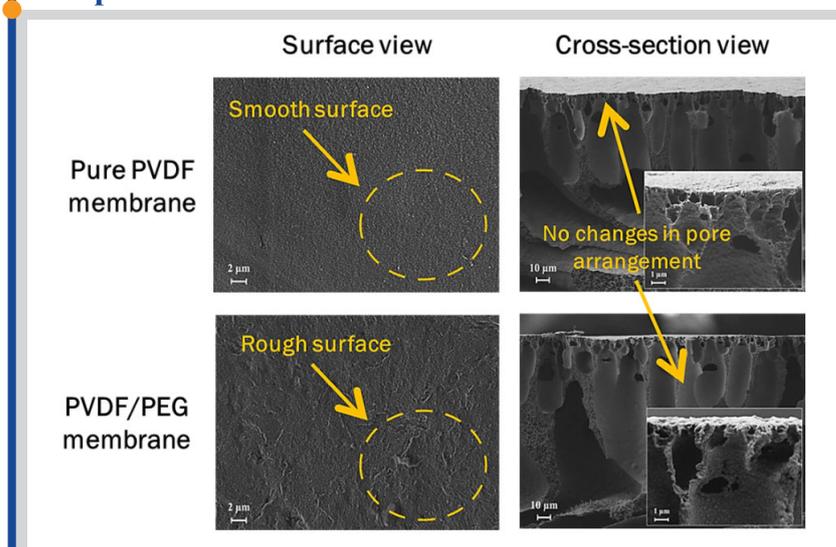
Abstract

Palm oil mill effluent (POME) treatment through fermentation under controlled conditions generates biogas with an equal volume of biohydrogen (H_2) and carbon dioxide (CO_2). The H_2 can be utilised for generating renewable energy through a hydrogen fuel cell. However, the existence of CO_2 at certain concentration might cause cell poisoning. Therefore, gas upgrading is required. Membrane technology has been identified as one of the best methods for gas upgrading owing to its excellent purification performance. In this study, polyvinylidene difluoride (PVDF) membrane was synthesized at various polymer concentrations of 13-18 wt% through the phase inversion method before being coated with polyethylene glycol (PEG). From the results, the surface negativity and contact angle of the synthesised PVDF membranes were increased at higher PVDF concentration, therefore leading to increase in PVDF membrane's hydrophobicity. As there was an increase in the membrane's hydrophobicity, the membrane's selectivity towards H_2 increased as well, with the most H_2 purity noted at 85%, which was attained by PVDF18 membrane. On adding PEG on the membrane surface, hydrophobicity rose from 81° (pure PVDF) to 100.8° (PVDF-co-PEG10). Moreover, PEG coating on the surface of PVDF membranes has enhanced their selectivity with the highest value of selectivity of up to 3.3. The PVDF-co-PEG10 membrane also has the highest H_2 gas purity of up to 96% in comparison to pure PVDF membrane (only 85% H_2 purity). This finding proved that PVDF-co-PEG10 membrane possessed a higher preference in the H_2/CO_2 separation compared to pure PVDF membrane.

1. Introduction

The rising demand for energy has triggered the vast development and massive exploration towards gas separation technology for a more energy efficient. Biogas produced from the fermentation of biomass residues from agricultural products such as palm oil is considered as one of the promising alternative energy that can be utilised to produce electricity required in the fuel cell application [1]. Nonetheless, the main problem of using the biogas generated through palm oil mill processes was regarding its purity. Recognising the benefits of the biogas to the energy application, a research has been conducted to produce biogas with high amount of bio-hydrogen (H_2) and decrease other impurities in the biogas [2-4]. As per [5] and [6], treatment of Palm Oil Mill Effluent (POME) via fermentation under regulated conditions (dark fermentation using mixed culture at 55°C temperature, pH of

5.5 and 3 days of hydraulic retention time) could generate biogas which primarily consists of mixture of H_2 and carbon dioxide (CO_2) gas with an equal amount. The H_2 can be utilised as a source of clean energy for generating renewable energy through hydrogen fuel cells. However, the existence of CO_2 at certain concentrations might cause cell poisoning, and hence gas upgrading is required.

There are many well-known gas upgrading techniques deployed for purifying valuable/energy gases; these include absorption, adsorption and membrane methods [1,6,7]. The conventional absorption technique has been deployed for a long time on an industrial scale to eliminate CO_2. Nonetheless, several shortcomings like high energy intensive, flooding and serious equipment corrosion contributed to a chief operational problem [8]. Because of the high energy use and complex functioning of other technologies, membrane technology has been recognised as one of the best techniques for H_2 separation and purification [9,10]. Innovative gas membrane is required to serve the technology need like low capital cost, small environmental footprint, high energy efficiency and clean and easy operation. Membrane for gas separation can be synthesised from both organic and inorganic materials. Nonetheless, inorganic membrane is very expensive and it is also rather difficult to produce a defect-free/uniform inorganic membrane [11]. Thus, apparently, polymeric membrane is an attractive option for the process of biogas separation.

One of the appropriate polymers that can be regarded as a good option for separation of biogas is polyvinylidene fluoride (PVDF) and this has been the theme of active studies in polymer science; it has attract a large amount of attention in several membrane separations [12-14]. PVDF is a semi-crystalline polymer which has been extensively utilised in the gas separations because of its excellent chemical resistance, thermal stability and good mechanical characteristics [12,15,16]. This membrane is generally synthesised by the phase inversion method with or without addition of suitable additives like polyethylene glycol (PEG) in order to fulfil certain criteria. PEG is a linear polyether compound which is available in different molecular weights, and it is generally used for pore formations in porous membranes and as modifier in applications of gas separation membrane [17,18]. The flexible characteristics of the PEG chain have rendered them apt for CO_2 gas separation through the interaction of the polar CO_2 and the etheric oxygen atom in the chain of PEG. Hence, it could be useful to the membrane in providing an improved diffusivity of large penetrant of gas like CO_2. PEG could also regulate the membrane's total free volume by increasing the mobility of chain of the supporting polymer and thus often utilised as one of the plasticisers [19].

Several studies have been conducted by presenting PEG as an additive for the polymer in synthesising a membrane for the process of gas separation upon considering PEG to CO_2 separation's high selectivity [20]. Generally, the blending method was employed to incorporate the additive PEG with the polymer. As per Hamrahi and Kargari (2017) [21], the selectivity and permeability of the polycarbonate (PC)/PEG blended membrane reduced as there was an increase in the functional pressure and PEG content. It happened because of the changes in morphology (from non-porous to porous), thereby reducing the selectivity. Moreover, Bengtson et al. (2017) [22] have altered the membrane synthesised by using polymers of intrinsic microporosity (PIM-1) and mixing with PEGs of different molecular weights. After the alteration, an increase in the modified membrane's hydrophilicity has reduced the selectivity of CO_2 compared to the N_2 gas. The altered membranes were considered to be of use in other membrane applications like pervaporation and nanofiltration since there was an increase in the hydrophilicity of the membrane.

One potential way to prevent morphological changes in the pure PVDF membrane is through a simple alteration of the membrane matrices such as by modification of the surface in order to introduce various functions and enhance molecular structure of the membrane. Surface modification is regarded as a cost-effective method to render the cultivating characteristics to the membrane while retaining its bulk characteristic [23,24]. Nonetheless, it was rather difficult to effectively separate and purify H_2 from CO_2 gas mixture especially when molecular sieving is the primary separation mechanism for the membranes because of the propinquity in the molecular size differences for both gases (molecule kinetic diameter in case of H_2 is 2.89 Å, while for CO_2 it is 3.30 Å) [25]. Thus, it is very significant to determine an efficient polymeric membrane that can potentially be used for this purpose. In this study, several concentrations of suitable PVDF polymer were examined with respect to their hydrophobicity and separation characteristics. Then, surface modification using PEG was carried out to the membrane using dip-coating technique by altering PEG concentration. The modified membrane was then characterized with respect to its morphology and hydrophobicity. Lastly, the membrane's separation performance was examined with individual gas (H_2 and CO_2) and combined gases (50% H_2 and 50% CO_2).

2. Experimental method

2.1. Materials

The membrane polymer utilised was polyvinylidene fluoride (PVDF) Solef 6010 powder from Solvay, USA. For membrane modification, polyethylene glycol (PEG) having a molecular weight of 600 g/mol and supplied by Sigma Aldrich was utilised. To dissolve the polymer and PEG, analytical grade N-methyl-2-pyrrolidone (NMP) and 95% ethanol Friendemann obtained from Schmidt, Australia were used, respectively.

2.2. Fabrication of flat-sheet membranes

The PVDF membranes were synthesized at different polymer concentration via phase inversion method. Initially, the PVDF dope solution was prepared by weighing the desired weights of the PVDF powder (13 to 18 wt%) and the NMP solvent (87 to 82 wt%) (refer Table 1). Then, the NMP solvent was added into the conical flask that contained a magnetic stirrer bar and the weighted PVDF polymer. To prevent the evaporation of the solvent, parafilm and aluminium foil were used to seal the mouth of the conical flask tightly. Next, stirring of the mixture was done for 6 h at 200 rpm. The resulting mixture was then allowed to settle overnight to get rid of all the bubbles that were produced in the solution. The PVDF dope solution was then casted at 150 μm thickness using a casting machine (Elcometer 4340). For purposes of solvent exchange, the layer was immediately placed in a bath with 5 L of deionized water. The fabricated PVDF membrane was then set aside for overnight storage in fresh deionised water after 2 h. It is then dried at room temperature before utilisation.

2.3. Surface modification of flat-sheet membranes

The dip coating method was used to perform surface modification on the fabricated PVDF membrane using PEG. Preparation of varying concentrations of the PEG solution (10, 15, and 20 wt%) was done by dissolving the desired PEG weight in ethanol (refer Table 1). Prior to modification, the membrane was cut into a circle having a diameter of 4.9 cm, which was necessary for following the size of the permeation unit. The PVDF membrane was then instantaneously dipped into the PEG solution before undergoing a rinse using deionized water. Finally, drying of the modified membrane before utilisation was done at room temperature.

2.4. Characterization

2.4.1. Morphological property

The morphologies of the casted PVDF membranes (modified and pure) were observed using a high-resolution field emission scanning electron microscope (FESEM, SUPRA 55VP). Magnifications of 3.0 K and 0.5-10.0 K were used to view the surface and cross-section of the membranes, respectively. Both observations had to be placed at an EHT voltage of 3.0 k. Analysis of the membranes' surface composition was done using GV 10x DS Asher-EDX machine (ibSS, USA). The purpose of this analysis is to determine if the PEG layer is present on the membrane surface.

2.4.2. Chemical property

Analysis of the effect of PEG layer application on the chemical structures of PVDF membrane was conducted using Fourier transform infrared (FTIR, Nicolet 6700 Thermo-Fischer Scientific), having an attenuated total reflectance unit at a resolution value of 4 cm^{-1}. Scans for the wave numbers of 4,000-600 cm^{-1} were done 16 times, each with a scan time of 1 min.

To examine its hydrophobicity properties, measurement of the contact angle for the fabricated membranes was performed using Drop Shape Analysis (DSA100, Kruss GmbH; German). For measurement purposes, pure water served as the polar liquid. Using a micropipette, about 3 μL of the water droplet was dispensed onto the membrane's surface. Based on the measurements obtained from 3 separate droplets within a region of 5 mm x 5 mm, an average contact angle value was computed.

Analysis of the membrane surface negativity properties was conducted using a Malvern Zetasizer. Cutting of the membrane was done based on the size of the membrane holder. The resulting membrane was then attached to the holder using a double-sided tape. Then, the holder was immersed into a cuvette holding a latex solution of pH 7 before inserting the cuvette into the sample platform. The analysis was performed thrice in order to obtain the average value.

Table 1
The composition properties of fabricated and modified membrane dissolved in NMP.

Membrane Sample	Parameter	
	Polymer Concentration (%)	PEG Concentration (%)
PVDF13	13	-
PVDF15	15	-
PVDF18	18	-
PVDF/PEG10	18	10
PVDF/PEG15	18	15
PVDF/PEG20	18	20

2.4.3. Gas permeation test

A membrane permeability unit was used to measure gas permeability. Figure 1 illustrates the real image of the membrane permeability unit. Then, the fabricated membrane was cut into a circle having a diameter of 4.8 cm. The resulting membrane was then inserted into the membrane cell. A bubble flow meter was used to connect the permeation cell of stainless steel made. Measurement of the permeability of the membrane was performed at varying pressure values ranging from 0.5 to 1.5 bar using pure H_2 (99.5%) and CO_2 (99.8%) gas. Equation (1) below was used to calculate the permeability or pressure-normalised fluxes:

$$\left(\frac{P}{L}\right) = \frac{Q}{A\,\Delta P} \tag{1}$$

where $\left(\frac{P}{L}\right)$ is the ideal gas permeability (GPU), Q is the volumetric flow rate of gas (cm/s), A is the surface area of membrane (cm^2) and ΔP is the pressure of gas (cmHg). Meanwhile, the ideal separation factor (α) of the gas separation membrane can be calculated using equation (2):

$$\alpha = \frac{\left(\frac{P}{L}\right)_{H2}}{\left(\frac{P}{L}\right)_{CO2}} \tag{2}$$

2.4.4. Membrane separation performance

Membrane separation performance test was performed using a gas mixture made up of 50% H_2 and 50% CO_2 as the feed gas. The gas mixture's composition mimicked that of the real biogas mixture that was obtained using POME fermentation as reported in [1, 5]. Analysis of the percentage of the rejected gases was done using a CO_2 analyser (Model 906, Quantek Instrument, USA).

2.4.5. CO_2 plasticisation effect on membranes

The CO_2 plasticisation effect is a common phenomenon that takes place in polymeric membrane during the process of gas separation process. This effect is responsible for the loss of membrane selectivity. Plasticisation takes place in most polymer membranes under specific pressure and CO_2 concentration [26]. The membrane's CO_2 plasticization was examined in terms of pressure effect. Varying pressure values ranging from 1 to 4 bar were utilised for flowing pure CO_2 and H_2 gas within the membrane permeation unit. The effect of plasticization is observable at the point where there is sudden increase in the permeability of the gases.

3. Results and discussion

3.1. Effect of polymer concentration on membranes properties

Polymer concentration can be seen as one of the most vital factors in tailoring a membrane since it has the ability to greatly influence membrane porosity. This is especially important since molecular sieving is seen as the primary separation mechanism to the gas membranes. Thus, evaluation of the characteristic of the synthesised polymeric PVDF membranes under varying polymer concentrations (13, 15 and 18 wt%) was conducted in terms of surface negativity, membrane hydrophobicity, and filtration performances.

The determination of the hydrophobic characteristics of the membranes was made by ascertaining the contact angle between the water droplets while zeta potential was used to determine the negativity of the membrane surface. As shown in Figure 2, an increase in the polymer concentration in the PVDF membranes led to an increase in the surface negativity and the contact angle, thereby causing the PVDF membrane to have a higher hydrophobicity. A membrane with greater hydrophobicity attributes is much favourable for CO_2 removal. This is due to the fact that CO_2 is not forced to diffuse through the membrane and hence could enhance the separation performance [27]. The results indicated that the PVDF18 membrane, which has an 18 wt% concentration of polymer, has the maximum contact angle. For this study, 18% is the highest used concentration. As the polymer concentration increase beyond 18%, it led to the agglomeration of the dope solution causing defects to the membrane. Ahmad et al. reported a similar observation, and their study concluded that defect-free polymeric gas membranes could be produced with a polymer concentration range of 13 to 19 wt% [28]. Hence, for this research, PVDF18 membrane having an 18 wt% concentration is chosen due to its efficiency of gas separation, which can be attributed to its high hydrophobicity.

Next, the casted membranes were evaluated with regards to their filtration performance with changing pressure. Figure 3(a) depicts membrane permeability in the case of individual gases (H_2 and CO_2). Consider all the membranes, and it was observed that the PVDF13 membrane had the highest permeability concerning H_2 and CO_2 at 0.5 bar pressure; the permeability values were up to 1,530 and 760 GPU, respectively. In contrast, the PVDF18 membrane was found to have the lowest permeability in both gases. It was noted that as the polymer concentration rose, the permeability of the membrane reduced. This is because of the augmentation in dope solution viscosity when polymer concentration was raised [16]. It was established that a high-viscosity dope solution would cause high mass transfer resistance in the course of phase inversion, thereby leading to the generation of a denser and tightly packed membrane [28,29]. A denser top layer influences membrane permeability because of the increased mass transfer resistance through the membrane. Therefore, the reason that attributed to the decrement of PVDF membrane permeability as polymer concentration increased can be relate to its porosity. Additionally, fabricated membranes have distinct thickness because of the use of different polymer concentration during the preparation of the dope solution. The PVDF18 membrane, with a thickness of 119.2 µm, has the thickest cross-section. PVDF15 is second with 113.4 µm membrane thickness, while for PVDF13, the value is 111.2 µm. Typically, a thicker membrane having lesser porosity is produced when the dope solution has a high concentration of polymer [10,30,31]. These findings are in line with the results of this study.

Another notable trend in this work is that the permeability value for H_2 gas was always greater compared to the CO_2 permeability. This phenomenon occurred because of the differences in the gases' molecular size. The molecular size of H_2 gas (2.9 Å) was smaller compared to CO_2 gas (3.3 Å) which aided the H_2 gas to effortlessly permeate through the membranes [6, 32]. At the same time, the membranes presented an increased resistance to CO_2 gas because of the larger sized molecule and, therefore, low permeability was observed, as depicted in Figure 3(a). In terms of the pressure characteristics, for every membrane, during filtration indicate a reduction in permeability when the pressure is increased. The observation could probably be attributed to the effects of competitive solubility between the polymer matrix and the gas. The measurement done at high pressure leads to zero swelling effect, while membrane compaction causes the gas permeability to reduce [6,21,33].
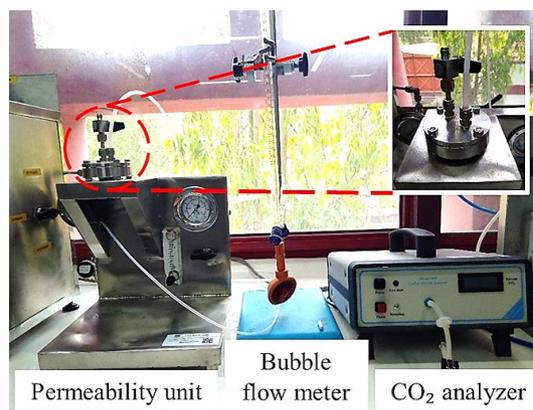

Fig. 1. Real image of membrane permeability unit.

In spite of the decreased permeability at high-pressure conditions, an increase in selectivity was observed for all the membranes, as depicted in Figure 3(b). The PVDF18 membrane was found to have the highest selectivity at 1.5 bar pressure. In contrast, the lowest selectivity was observed using the PVDF13 membrane at 0.5 bar pressure. The trend indicates that membrane selectivity towards H_2 and CO_2 gases rose proportionally to pressure and polymer concentration. The result showed that the PVDF18 membrane provided the comparatively purest form of H_2 gas, where the separation level was 80%, as depicted in Figure 4. On the other hand, the PVDF15 and PVDF13 membranes were found to have lower H_2 gas purity recorded at 56% and 54%, respectively. It is clear from the results that an increased polymer concentration leads to a membrane having high resistance to gas diffusivity, thereby leading to reduced purification efficiency. In general, the PVDF18 membrane exhibited the highest H_2 gas purification potential because of its favourable characteristics like better hydrophobic property and better selectivity to the separated gases.

3.2. Effect of PEG concentration on membrane properties

With intent to enhance the molecular selectivity of the membrane, a PEG coating was applied to the surface of the PVDF membrane. PVDF18 was selected for the experiment since it has high selectivity towards the separation of CO_2/H_2 gases. Meanwhile, PEG was selected for membrane modification because of its flexibility and high diffusion potential for large-sized penetrant like CO_2 (it has been investigated in the study) [20,34]. Additionally, previous research indicates that using PEG with the polymer leads to the membrane having higher hydrophilicity, promote pore formation as well as decline its tensile strength. These characteristics significantly alter the PEG-blended polymer membrane [35-39]. Porous membranes are found to have high flux for gas separation; however, they are less selective in nature [40]. In order to prevent the formation of pores over the pure PVDF membrane, the PEG layer was formed using the dip-coating method. Effects of varying PEG concentration (10, 15, and 20 wt%) on the characteristics of the membrane were evaluated with a focus on surface negativity, separation performance, and hydrophobicity. These parameters were compared against the values obtained for a pure PVDF membrane (originally produced from the PVDF18 membrane).

The plots for contact angle and zeta potential exhibited by the PVDF-co-PEG membrane and their comparison with pure PVDF membrane are depicted in Figure 5. In theory, membranes having a contact angle less than 90° can be classified as a hydrophilic membrane, while those having a larger angle are classified hydrophobic [41]. The results clearly indicate that the pure PVDF membrane may be classified as hydrophilic, given the contact angle is less than 90°. The value of the contact angle rose sharply to 100.8° when the surface of the membrane was modified using 10% PEG, thereby indicating a rise in hydrophobicity. Nevertheless, with the PEG concentration reaching 15% and 20%, a reduction in contact angles was observed with the values being 91.4° and 81.1°, respectively. This decrease in the contact angle with increasing PEG concentration was expected, given the hydrophilic nature of PEG [37,42]. This increase in membrane hydrophobicity/hydrophilicity impacted penetration performance because of the varying diffusivity across membranes.
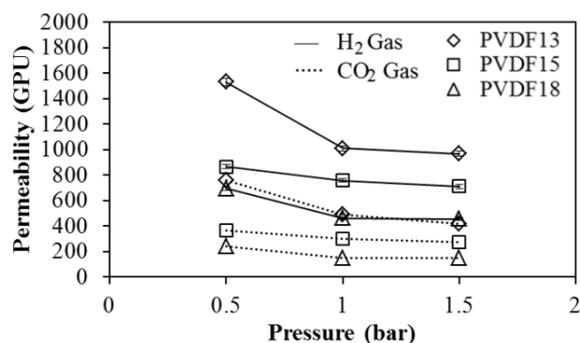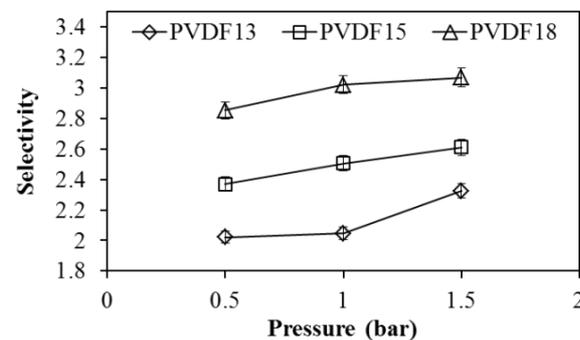
**Fig. 3.** (a) Permeability on single gas and (b) selectivity for PVDF membranes at different pressure
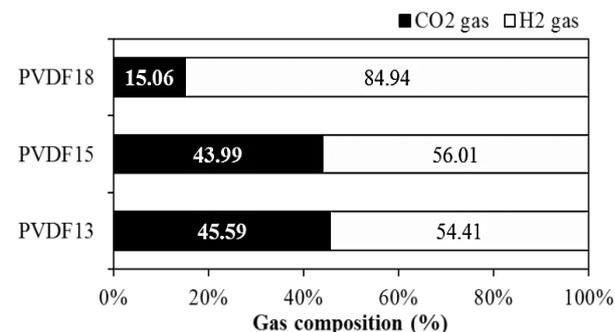
Fig. 4. Composition of H_2 and CO_2 after permeation test at pressure 1.5 bar by using PVDF membrane casted at different polymer concentration.
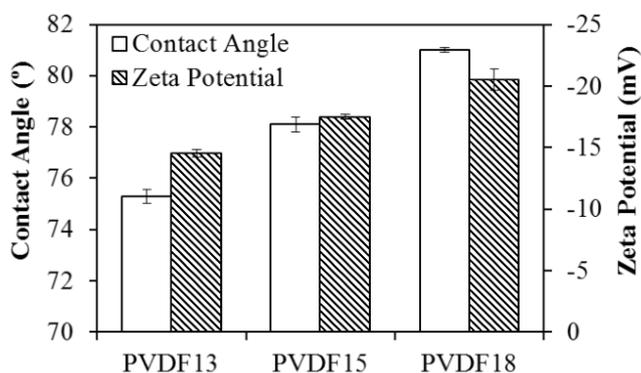
Fig. 2. Contact angle and zeta potential for PVDF membranes casted at different polymer concentration
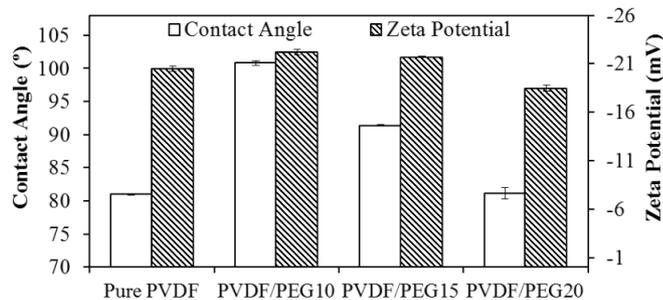
Fig. 5. Contact angle and zeta potential for PVDF/PEG membranes at different concentration of PEG in comparison with unmodified membrane.

Moreover, the modified membranes exhibited a slight decrease in permeability, as depicted in Figure 6(a). Nevertheless, a comparison with varying PEG concentrations demonstrated an increasing trend with an increase in PEG concentration. This increase may be correlated with the increase in membrane hydrophilicity. Additionally, there was a reduction in membrane selectivity when the PEG concentration increased, as depicted in Figure 6(b). Hence, the result further establishes the significant role of hydrophobicity in membrane selectivity and permeability. Still, the modification of the membranes by using a PEG layer on their surface led to better membrane selectivity, particularly in the case of the PVDF/PEG10 membrane, where the highest selectivity up to 3.3 was obtained. Additionally, the PVDF/PEG10 membrane has the highest H_2 gas purity of up to 96%, as shown in Figure 6(c) if compared to pure PVDF membrane with the highest purity obtained at 85% only. The result indicates that a PEG-modified PVDF membrane exhibits higher preferential separation of H_2/CO_2, when compared to an unmodified PVDF membrane.
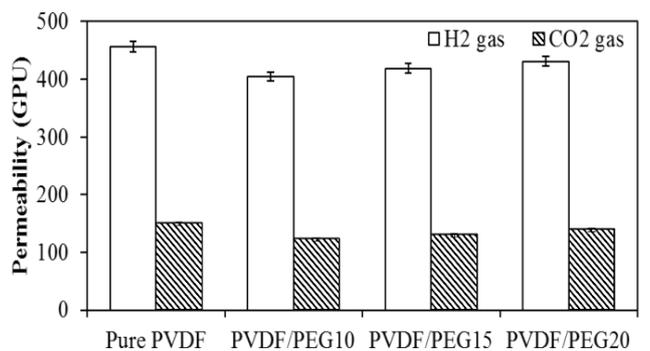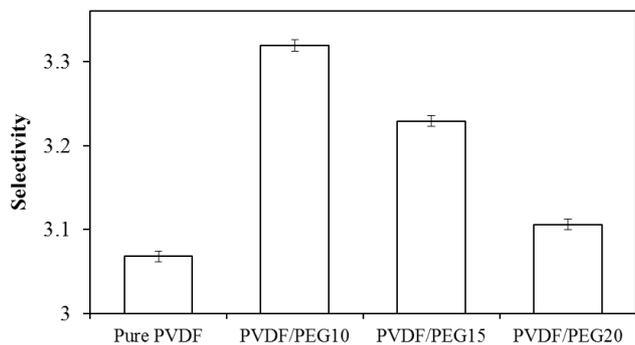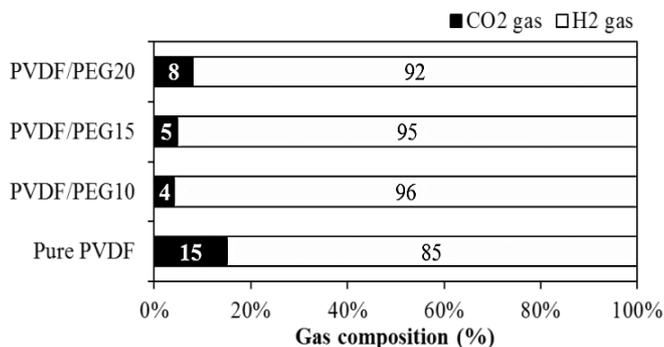
3.3. Evaluation of membrane performance

Considering the superior selectivity of the PVDF/PEG10 membrane to CO_2 compared to other membranes, further assessment of the current membrane was undertaken, and the attributes were compared with those of a pure PVDF membrane. The performance assessment for the membranes was conducted by studying how plasticisation pressure affected the membranes (pressure range was 1 to 4 bar). A polymeric membrane typically exhibits plasticisation during gas separation [25]. It is crucial to determine the extent of plasticisation for practical applications because membrane selectivity is directly impacted. Figure 7 depicts the selectivity and permeability of the pure and modified form of the PVDF membrane under high permeation pressure. A decreasing trend with regard to permeability was observed for both membranes when applied pressure was raised. Nevertheless, after reaching a specific pressure, an increase in permeability was observed. For instance, the PVDF/PEG10 was found to have enhanced permeability for H_2 and CO_2 at a pressure of 4 bar. In the case of the pure PVDF membrane, the permeability increased for H_2 and CO_2 started at pressure values of 4 bar and 3 bar, respectively. These findings indicated that plasticization effect was detected at the investigated pressure range for both membranes. The results indicate that the modified PVDF-co-PEG membrane is quite superior to the pure PVDF membrane since the modified form exhibits plasticisation at a comparatively higher pressure (4 bar), which for the pure form starts at 3 bar.

The PVDF/PEG10 membrane demonstrated a comparatively higher selectivity than the pure PVDF membrane at all applied pressure. Membrane selectivity increased with pressure, but it began to decrease at a pressure of 4 bar (as shown in Figure 7(b)). In contrast, the selectivity of the unmodified PVDF membrane began to decrease at a lesser pressure value of 3 bar, thereby indicating that the PEG coating provides superior properties to the membrane in the form of an increased selectivity for CO_2/H_2 separation while maintaining selectivity at higher operating pressure. The development of the PEG layer over the PVDF membrane could perhaps be the primary reason behind the enhancement of the plasticization effect. On top of that, the CO_2 absorption also increased as discussed in section 3.2 since PEG was proven to have the ability to diffuse a large penetrant such as CO_2.

(a)

(b)

(c)

Fig. 6. (a) Permeability on single gas, (b) selectivity and (c) H_2/CO_2 composition at pressure 1.5 bar for PVDF/PEG membranes at different concentration of PEG in comparison with unmodified membrane.
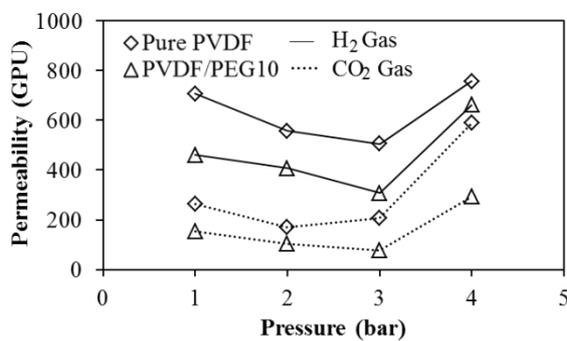
(a)
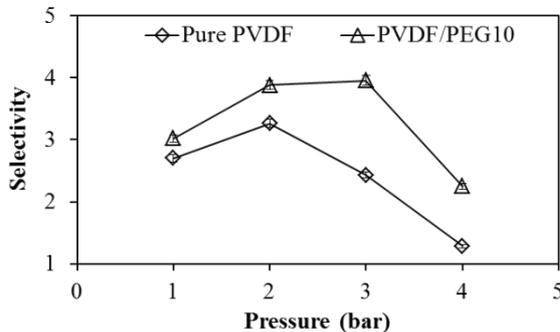
(b)

Fig. 7. (a) Permeability on single gas and (b) selectivity at different pressure plasticization effect study.

Membrane characterisation was performed to establish that a PEG layer has been successfully deposited on the surface of the PVDF membrane. The modified and pure membranes were characterised with regards to their morphology and chemical characteristics. Figure 8 depicts the FESEM images (cross-section and surface view) and the EDX analyses for the fabricated membranes. The images indicate that the morphology of either form of the PVDF membranes did not exhibit noticeable changes, especially regarding pore arrangement. Interestingly, a white layer is clearly visible on the modified membrane surface (as depicted in Figure 8(d)), which may be caused by the PEG layer. Additionally, it is clear from the EDX spectra that a new chemical element is present post PEG coating. Oxygen (O) is identified as the new element, and it was absent in the pure PVDF membrane. The chemical structure of PVDF comprises alternating $C-F_2$ and $C-H_2$ bonds. Oxygen is present in the PEG $(H-(O-CH_2-CH_2)_n-OH)$. Therefore, EDX analysis establishes that a PEG layer is present on the modified PVDF membrane, thereby validating that the observed changes in permeability, selectivity, and CO_2/H_2 separation were indeed caused by the PEG layer.

4. Conclusions

The pure form - PVDF18 membrane (prepared using 18 wt% polymer) exhibited the highest selectivity compared to those prepared using 13 and 15wt% concentrations. The membrane hydrophobicity was also increased as the polymer concentration increased, thereby leading to betterment in separation performance, where the maximum obtained purity of H_2 was 85%. The PVDF18 membrane was further enhanced using different PEG concentrations (10-20%). As a result, the contact angle for the PVDF/PEG membrane exhibited an increase from an initial 81° to 100.8° after modification. Nevertheless, a reduction was observed with further increase in PEG concentration, thereby suggesting enhanced membrane hydrophilicity. Hence, membrane selectivity and separation performance saw a minute reduction from 96% (10% PEG) to 92% (20% PEG). Thus, the PVDF membrane having 10% PEG (lowest) was selected because of the highest selectivity, superior separation performance (CO_2 from H_2), and superior plasticisation tolerance.
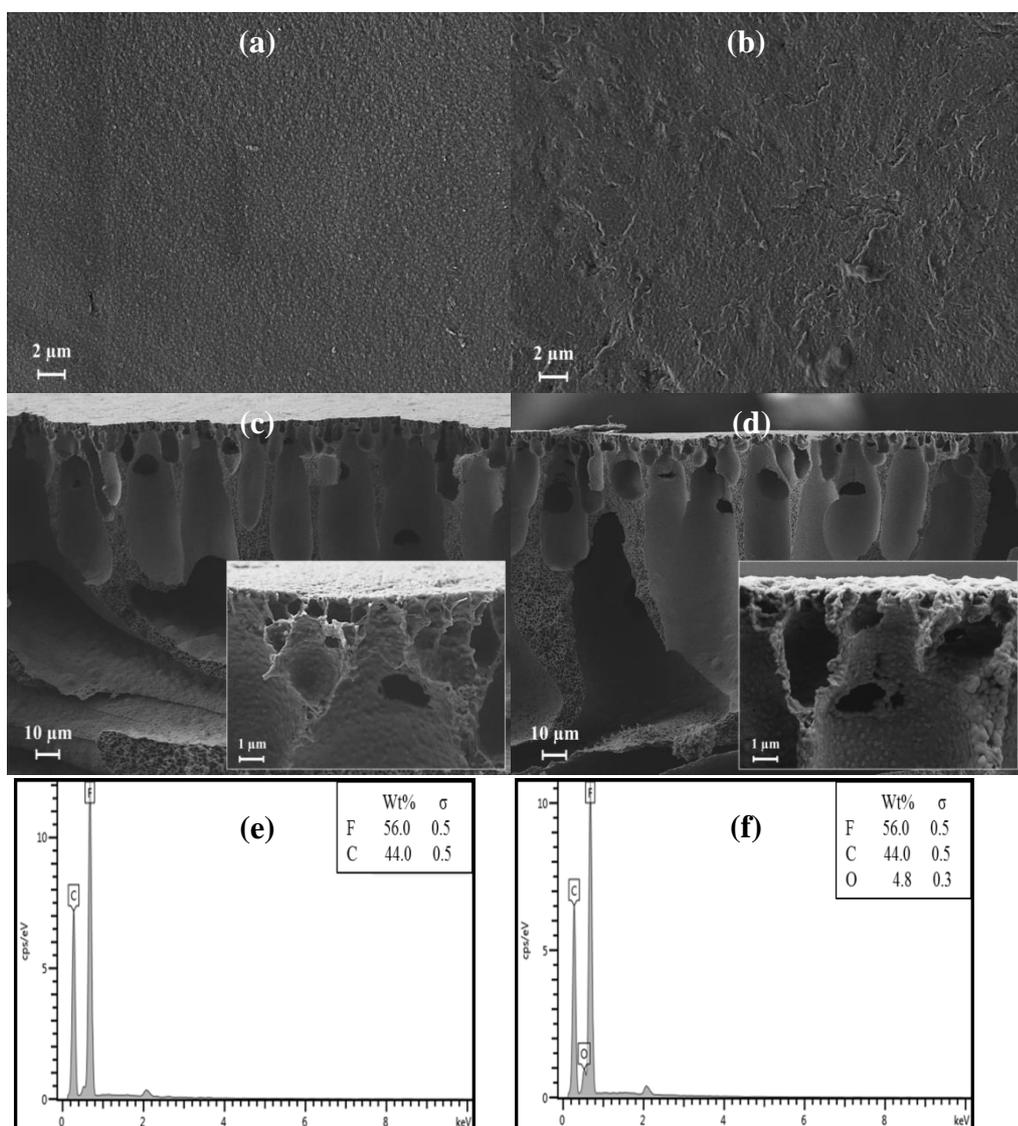
Fig. 8. FESEM images with top surface view: (a) pure PVDF membrane, (b) modified membrane; cross-section view: (c) pure PVDF membrane, (d) modified membrane; EDX analysis: (e) pure PVDF membrane, (f) modified membrane.

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