



ORIGINAL ARTICLE

High performance of PES-GNs MMMs for gas separation and selectivity



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CO₂/CH₄ selectivity

Abstract In this study, graphene nanosheets (GNs) were incorporated into polyethersulfone (PES) by phase inversion approach for preparing PES-GNs mixed matrix membranes (MMMs). To investigate the impact of filler content on membrane surface morphology, thermal stability, chemical composition, porosity and mechanical properties, MMMs were constructed with various GNs loadings (0.01, 0.02, 0.03, and 0.04 wt%). The performance of prepared MMMs was tested for separation and selectivity of CO₂, N₂, H₂ and CH₄ gases at various pressures from 1 to 6 bar and temperature varying from 20 to 60 °C. It was observed that, compared to the pristine PES membrane, the prepared MMMs significantly improved the gas separation and selectivity performance with adequate mechanical stability. The permeability of CO₂, N₂, H₂ and CH₄ for the PES + 0.04 wt% GNs increases from 9 to 2246, 11 to 2235, 9 to 7151, and 3 to 4176 Barrer respectively, as compared with pure PES membrane at 1 bar and 20 °C due to improving the membrane absorption and porosity. In addition, by increasing the pressure, the permeability and selectivity of CO₂, N₂, H₂ and CH₄ are increased due to the increased driving force for the transport of gas via membranes. Furthermore, the permeability of CO₂, N₂, H₂ and CH₄ increased by increasing the temperature from 20 to 60 °C due to the plasticization in the membranes and the improvement

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in polymer chain movement. This result proved that the prepared membranes can be used for gas separation applications.

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1. Introduction

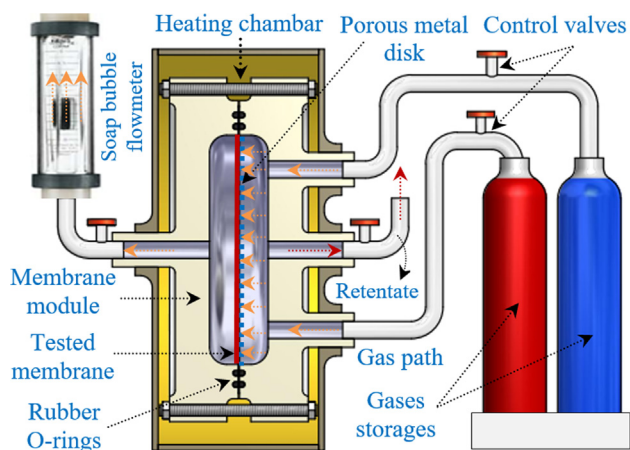
Worldwide energy demand is predicted to rise because of continued economic progress and a growing global population. As a result, greenhouse gas emissions such as carbon dioxide, methane, and nitrous oxide will be increased (Martin-Gil et al., 2019; Juber et al., 2021). According to the World Meteorological Organization (WMO), carbon dioxide levels in the atmosphere reached 393 ppm in 2012, an average increase of 2 ppm per year over the previous ten years (Wong et al., 2021; Yousef et al., 2021). In addition, CO₂, which is a pollutant in natural gas wells, lowers the energy content of the gas and becomes acidic and caustic in the presence of water, carbon dioxide/methane separation is critical for natural gas processing. Traditional CO₂ capture methods (such as cryogenic distillation and amine-based absorption) consume a lot of energy (Castro-Muñoz et al., 2020; Asif et al., 2021). Therefore, a cost-effective, efficient, and environmentally friendly capture process is required.

Among numerous technologies, membrane technology has attracted great attention in water and gas separation due to its highly competitive energy prices and environmental issues (Khalil and Schäfer, 2021; Mohamed et al., 2020). Currently, the removal of CO₂ and acidic gases from natural gas is carried out on a large-scale using the membrane separation process. Polyethersulfone (PES) is the most widely used material for the preparation of ultrafiltration (UF) and nanofiltration (NF) membranes for the gas separation process due to its strong mechanical, thermal, and chemical stability, as well as the fact that the inclusion of an ether unit in the polymer provides an alternative binding mechanism for CO₂ molecules (Abdel-Karim et al., 2018; Alenazi et al., 2017). The phase inversion process developed for the manufacture of polymeric membranes that are commercially viable and reproducible (Castro-Muñoz et al., 2018). These membranes possess have a skin layer on the top, followed by a porous sublayer, which

achieved high permeability and selectivity (Sazali et al., 2019; Yousef et al., 2022). The pore size of the polymeric membranes is greatly affected by external forces due to the deformation of the polymer material under high pressure and elevated temperature (Tan and Rodrigue, 2019; Mohamed et al., 2016). Mechanical properties of the membrane depend on the polymer properties and the pore topology (Karim et al., 2018; Salama et al., 2018). Hence, to increase the mechanical strength and enhance membrane performance, polymeric membranes have been incorporated into a variety of nanomaterials with sufficient properties (physical, morphological and permeation characteristics) to improve their efficiency for gas applications, such as TiO₂ (Tran et al., 2020; Yu et al., 2020), MOF (Daglar et al., 2021; Yang et al., 2020), SiO₂ (Kang, 2020; Arjunan et al., 2020), GO (Shukla et al., 2017; Ouyang et al., 2015), and CNTs (Cao et al., 2020; Mohamed et al., 2017).

Graphene nanosheets (GNs) have attractive great properties such as high surface area and high hydrophilic behavior in gas separation and water treatment in the fabrication of mixed matrix membranes (MMMs) (Fatemi et al., 2020; Gontarek-Castro et al., 2021). The main important feature of the GNs membrane is the interlayer spacing between the GNs sheets that can be tailored for efficient transport of the desired molecules through the membrane (Abdel-Mottaleb et al., 2019; Castro-Muñoz et al., 2019). In addition, GNs based membrane materials have high mechanical strength and flexibility, as well as high stability in aqueous suspension owing to the presence of the functional groups such as carboxyl, carbonyl, hydroxyl, and epoxy groups (Luque-Alled et al., 2020; Abdel-Mottaleb et al., 2019). These behaviours are very important in the preparation of homogeneous membranes for gas separation (Nair et al., 2012; Li et al., 2013). For instance, Gotthold et al. (Shin et al., 2019) incorporated GO into PES membrane for the selectivity of water-ethanol separation. The results showed excellent H₂O/EtOH selectivity and the membrane can effectively separate water-contaminated biofuels and the same for Geim (Nair et al., 2012) used for water-helium separation. Roberto et al. (Castro-Muñoz et al., 2019) combining graphene oxide into cross-linked PVA membranes to achieve better performance for ethanol dehydration. Moreover, the effect of filler dispersion in the polymer matrix to reach a synergistic effect has been addressed by Roberto et al. (Castro-Muñoz and Fila, 2019). The preparation of Matrimid®-PEG 200 and ZIF-8 nanoparticles have been demonstrated. The result shows that the incorporation of 30 wt% ZIF-8 nanoparticles allowed to increase the CO₂ permeability in MMMs. Srabani et al. showed that the incorporation of Mg-MOF-74 into PVAc enhanced the CO₂ separation (Majumdar et al., 2020). Furthermore, the addition of PEG and ZIF-8 enhanced the CO₂ permeability (Castro-Muñoz et al., 2019).

Nanostructured fillers help to reduce the shortcomings of polymer-based membranes such as aging, plasticization, and stability (e.g., physical, chemical, and thermal). However,



Scheme 1 (a) Schematic of the gas permeation set-up.

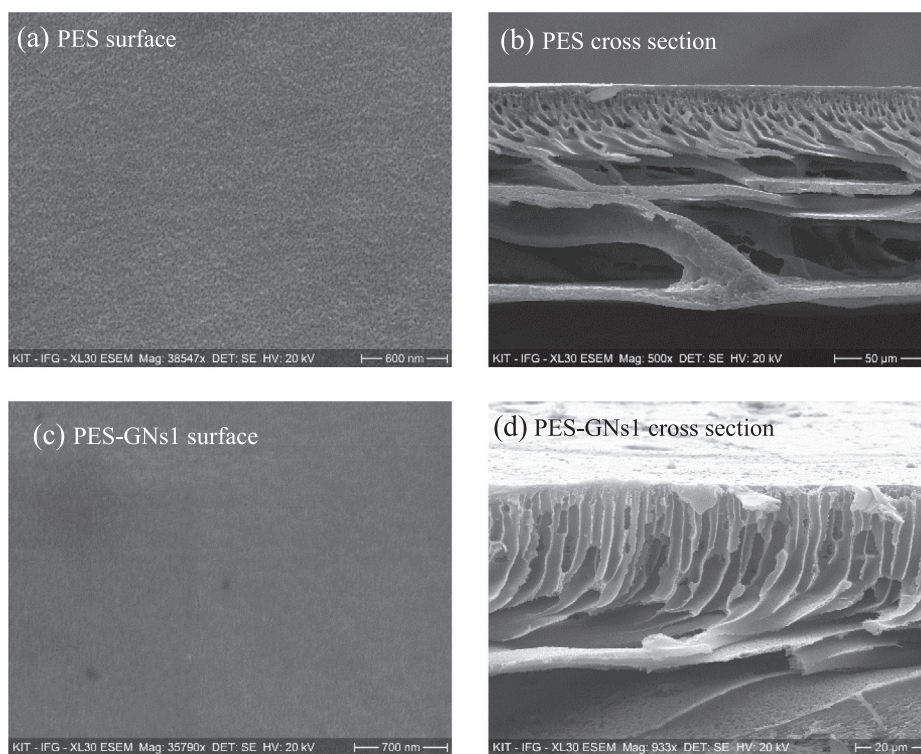


Fig. 1 Surface morphology and cross-sectional of a, b) PES, c, d) PES-GNs1, e, f) PES-GNs2, g, h) PES-GNs3 and I, j) PES-GNs4. K) pore size and porosity of membranes.

improper merging, such as poor interface compatibility and membrane preparation process, causes particular flaws in the filler–polymer membranes, such as new non-selective gas transport channels, which enhance permeability but impair selectivity (Castro-Muñoz et al., 2017; Ahmad et al., 2020). Ultrathin inorganic membranes prepared from the nanosheets have been identified as good candidates for producing higher performance membranes while using less inorganic nanomaterials, which is one of the key advantages of this type of membrane (Mohamed et al., 2021). There are a few other advantages to using ultrathin membranes: selective-layer materials in tiny quantities, resulting in significant material cost reductions; an optimized membrane material and morphology in each layer; minimal constraints on membrane materials’ mechanical qualities and processability as long as they can be produced or deposited as a thin layer on top. Membrane cost and permeance are both favored when membrane thickness decreases (Castro-Muñoz et al., 2020; Ahmad et al., 2021).

Biogas applications are typically composed of numerous gases mixed with flammable gases such as CO_2 , N_2 , and CH_4 . Which negatively affects the performance and economic value of the energy product and the separation process. The primary contamination sources in biogas are agglomerates, which tend to cluster together because of the force of attraction between particles gases, resulting in the formation of numerous agglomerate particles and significant pipe issues, such as corrosion. In this regard, the MMMs were developed to overcome these issues. In the literature, different studies show that the percentage of loading of NPs into the polymer are in the range of 0.5–15 wt% (Ismail et al., 2011; Yousef et al., 2021). At higher loading, NPs started to agglomerate and block the membrane pores as well as inhibit gas

transportation across the produced membranes, resulting in decreased membrane lifespan and high operating costs (Parsamanesh et al., 2021). But in our work, we used only 0.04 wt% with a high gas permeability. The main objective of this paper is to prepare a pristine PES membrane as well as mixed matrix membranes incorporated with different loading of GNs by a phase inversion approach. The performance of the prepared membranes is tested for separation and selectivity performance of CO_2/CH_4 , CO_2/N_2 and CO_2/H_2 under high pressure and elevated temperature. The physical and chemical properties of the developed membranes are characterized. The influence of the membrane deformation was also studied.

2. Experimental

2.1. Materials

Polyethersulfone (PES, Ultrason E 6020P) was purchased from BASF Company (Germany). Polyvinylpyrrolidone (PVP, $M_w = 40,000 \text{ g mol}^{-1}$) and *N,N*-Dimethylformamide (DMF, 99.8% purity) was supplied from Sigma Aldrich. GNs (95% purity, average thickness 15 nm, and average length 2 μm) were fabricated as described elsewhere (Yousef et al., 2018). CO_2 , N_2 , H_2 , and CH_4 gases with purity $\geq 99.99\%$ were supplied by the Lithuanian Energy Institute, Lithuania.

2.2. Membrane preparation

The pristine PES membrane and four mixed matrix membranes incorporated with different loadings of GNs

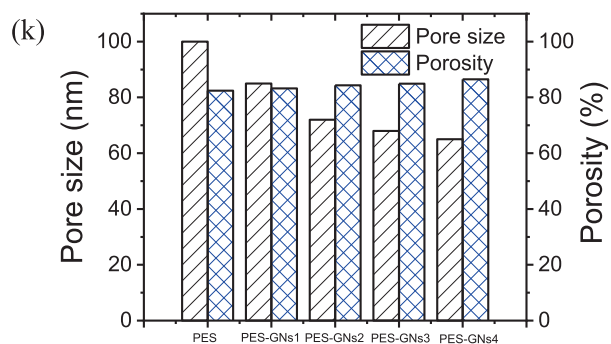
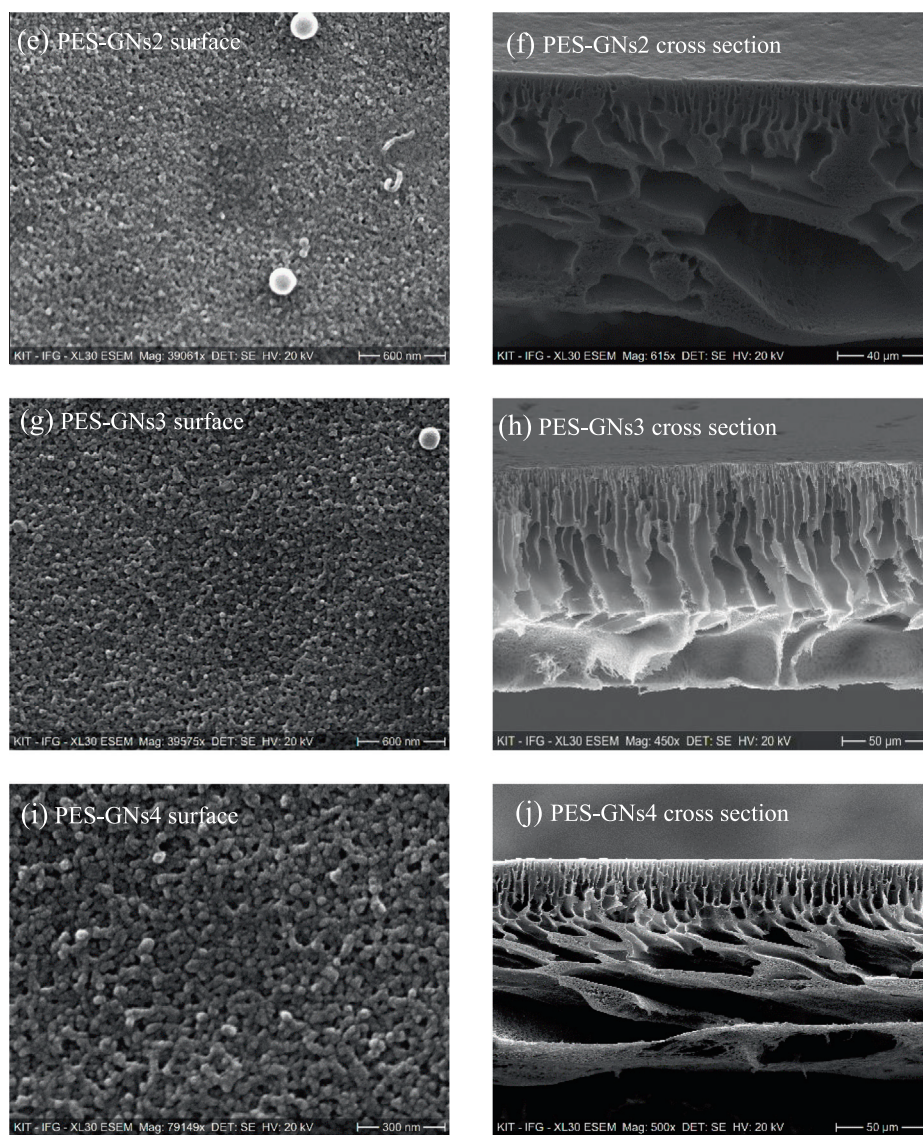


Fig. 1 (continued)

(0.01, 0.02, 0.03, and 0.04 wt%) were fabricated using the phase inversion technique. The homogeneous solutions were prepared by dissolving 14 wt% PES and 1 wt% PVP in DMF at 50 °C for 6 h. After degassing, the solutions were cast on a glass substrate using a casting blade (ZAA 2300, Germany) with a 100 μm gap height and 20 mm/s shear rate

(Yousef et al., 2021; Gouveia et al., 2021). The membranes were immediately immersed into a coagulant bath containing deionized water at 70 °C for 10 min and subsequently, the membranes were detached from the glass surface and transferred to a fresh deionized water for 24 h at room temperature to remove the excess solvent (Mohamed et al., 2021). After

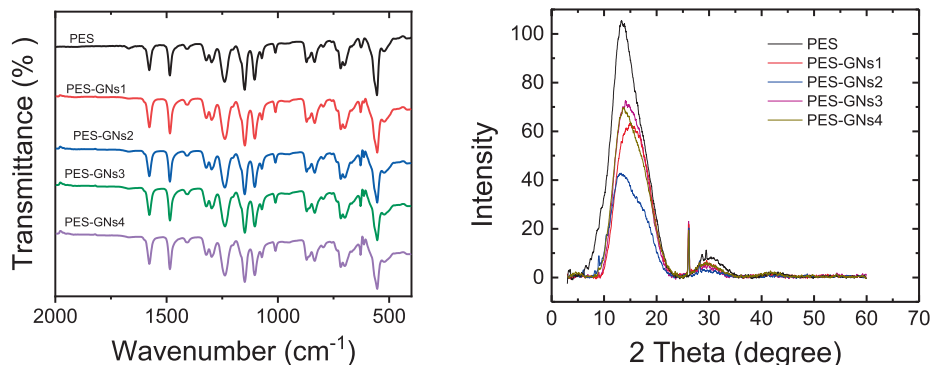


Fig. 2 a) FTIR and b) XRD spectra of the prepared MMMs.

that, the membranes were dried at room temperature. For the MMM, the GNs was added to the homogeneous solutions and then followed the same procedure.

2.3. Gas permeation test

In order to determine the separation and selectivity of CO_2/CH_4 , CO_2/N_2 and CO_2/H_2 , the permeability test was applied under various pressure and temperature. The experiments were performed in a gas permeation system using a circular membrane with an effective diameter of 60 mm (see Scheme 1). The membrane was supported into the cell and gently tightly and evacuated using a vacuum pump to remove all remaining gases from the cell. Before each gas experiment, the same procedures were done. The feed flow of each gas was passing through the membrane by adjusting the pressure from 1 bar to 8 bar at different temperatures in the range of 20–60 °C. All measurements have been made triple and the average values are recorded. The gas permeability ($P_{i,j}$) and membrane selectivity (α) were calculated according to Eqs. (1) and (2)

$$P_{i,j} = \frac{Q * t}{A * \Delta P} \quad (1)$$

$$\alpha_{i,j} = \frac{P_i}{P_j} \quad (2)$$

where i refers to CO_2 and j represents N_2 or H_2 or CH_4 . Q is the gas flow rate (cm^3/s), A is the membrane area (cm^2), t is the membrane thickness (cm), and ΔP is the transmembrane pressure difference (bar).

2.4. Characterization of the fabricated membranes

A field emission scanning electron microscope (FESEM, FEI Philips XL 30) was used to analyze the membrane's surface and the cross-section morphology. A thin coating of gold film (3–5 nm) was applied to all samples. The tests were made using a 20 keV acceleration voltage in a high vacuum (1.5 Torr). The thermal stability of the fabricated membranes was done using thermogravimetric analysis (TGA, Mettler Toledo TGA2 Star system) from 30 to 900 °C at a rate of 10 °C min^{-1} under a nitrogen environment. The chemical structures and composition of membranes were examined using the Fourier-Transform Infrared spectroscopy from 4000 to 400 cm^{-1} , 64 scans, and resolution 4 cm^{-1} (FTIR, Vertex70 spectrometer) and X-ray crystallography of 2θ from 3° to 60° with a 0.018–0.025° 2θ step width and 384 s per step for all samples (XRD, D8-Advance, Bruker, USA). Membrane porosity and pore size were measured by using mercury intrusion porosimetry (MIP, Pascal 440 Evo, Thermo Scientific). Tensile tests of the membranes were determined using Lloyd Universal Testing Machine (model LR10K) under ambient conditions and 5 mm/min loading rate. Three specimens 100 mm \times 10 mm from each membrane were cut off before the test.

3. Results and discussion

Fig. 1 demonstrates the surface morphology, porous structure and the cross section of the synthesized MMMs. Fig. 1a-e shows that the synthesized MMMs were uniform, smooth and homogeneous without obvious defects such as pores or

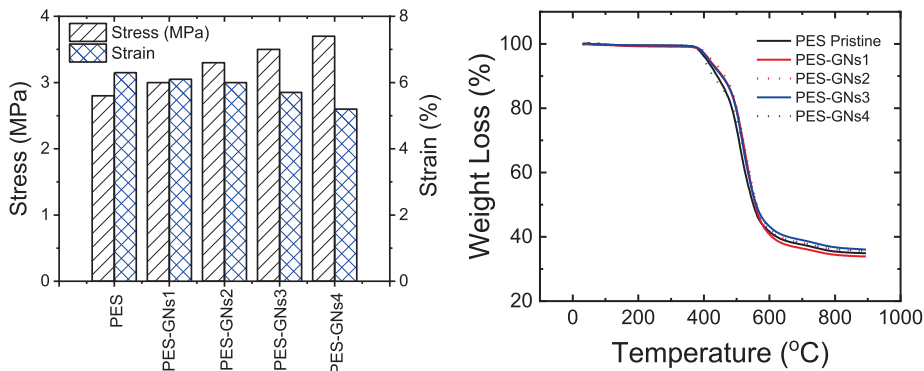


Fig. 3 a) Mechanical properties and b) TGA analysis of the prepared MMMs.

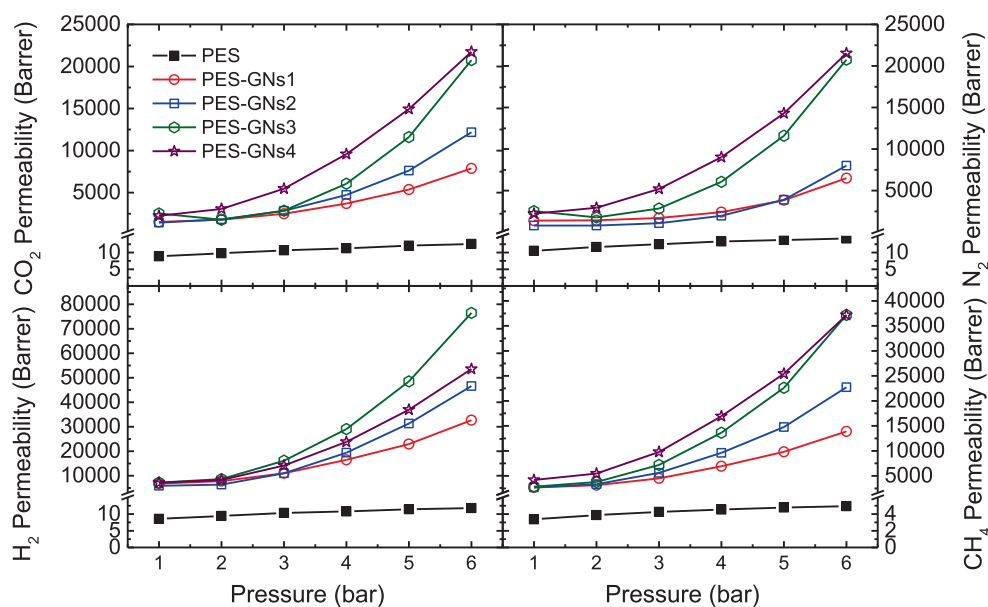


Fig. 4 Effect of feed pressure on CO₂, N₂, H₂ and CH₄ permeability values of the prepared membranes at 20 °C.

cracks. All the cross section membranes were prepared by being broken into liquid nitrogen. The cross-sectional images showed an asymmetrical structure consisting of a thin dense top layer and a porous sublayer with a macropores finger and mesoporous sponge structure underneath. The thin dense layer shows an infinite number of pores created during the preparation process, responsible for the permeation and retention of the solution. While the porous bulk acts as mechanical support. For the pristine PES membrane, there are smaller porous fingers and a decrease in the number of voids in comparison with the PES-GNs matrix membrane with a thickness of about 100 μm . This behaviour is attributed to the hydrophilic of GNs which improve the replacement of the water in the

phase inversion process. In addition, the pore size distribution of the prepared MMMs (Fig. 1k) decreased from 100 to 65 nm with increasing the GNs content. While the porosity increased with the incorporation of GNs from 82.4% for the PES membrane to 86.5% for PES + 4 wt% GNs which is in line with the analysis of the membrane morphology.

Fig. 2a shows the FTIR spectra of pristine PES membrane and PES with different loading of GNs. The result demonstrated that the FTIR of MMMs is largely indistinguishable from pristine PES, due to the limited amount of GNs. The result shows several broad absorbance peaks at 557, 1149 and 1296 cm^{-1} corresponding to the sulfone groups and at 1579 and 1485 cm^{-1} attributed to C = C skeleton in the

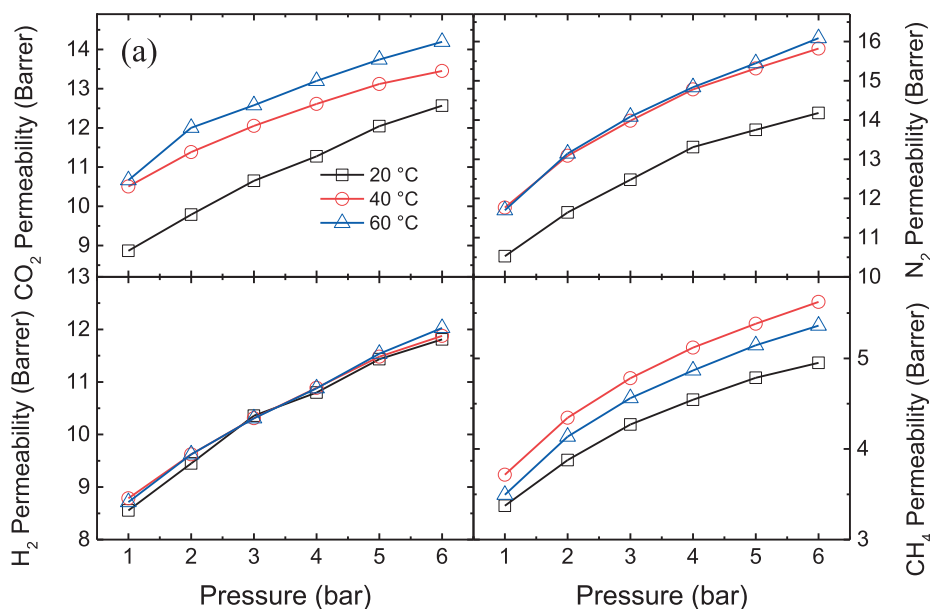


Fig. 5 Effect of different temperatures on CO₂, N₂, H₂ and CH₄ permeability values of the prepared membranes a) PES, b) PES-GNs1, c) PES-GNs2, d) PES-GNs3 and e) PES-GNs4.

aromatic rings (Shin et al., 2019; Abdel-Karim et al., 2017). The peaks at 1725 and 1668 cm^{-1} were assigned to the carbonyl group ($\text{C} = \text{O}$) and the two peaks at 1105 and 1238 cm^{-1} were attributed to C-O stretching vibration (Yousef et al., 2021; Angione et al., 2015). In addition, Fig. 2b shows the XRD spectra of pristine PES membrane and PES with different loading of GNs. The two peaks of the PES membrane are obvious at 2θ of 13.6 and 30°, indicating the amorphous nature of PES (Guan et al., 2005; Laghaei et al., 2016). In addition, for the MMMs another sharp peak is seen around 26.3° which is corresponding to GNs into the membranes (Mohamed et al., 2020).

The main criteria for membranes used in gas separation processes are strong mechanical properties to withstand high pressures in the gas permeation system (Aboamera et al., 2019). Therefore, to determine their mechanical properties, tensile strength experiments were conducted on the membranes. Experiments were performed by stretching the

specimen and measuring the instantaneous tension before the tearing at various strain rates. Fig. 3a shows the tensile stress and strain for the prepared MMMs samples. The result shows that incorporating of GNs improved the tensile strength of the MMMs in comparison to the pristine PES membrane. Furthermore, the tensile strength of MMMs is shown to be highly dependent on the loading of GNs. The pristine PES membrane showed 2.8 MPa tensile strength and by increasing the loading of GNs from 0 to 0.04 wt%, the tensile strength increased from 2.8 to 3.7 MPa with an increase of 32.14%. At the same time, the strain declined with increasing the amount of GNs, reaching a decrease of 17.46%. In addition, Young's modulus increased from 44.44 to 71.15 MPa with an increase of 60.1%. This behaviour may be attributed to the high strength properties of the GNs, good dispersion of GNs in the PES, and the improved interfacial interaction between the two phases (Abdel-Mottaleb et al., 2020; Li et al., 2019). Furthermore, the thermal stability of the prepared membranes was

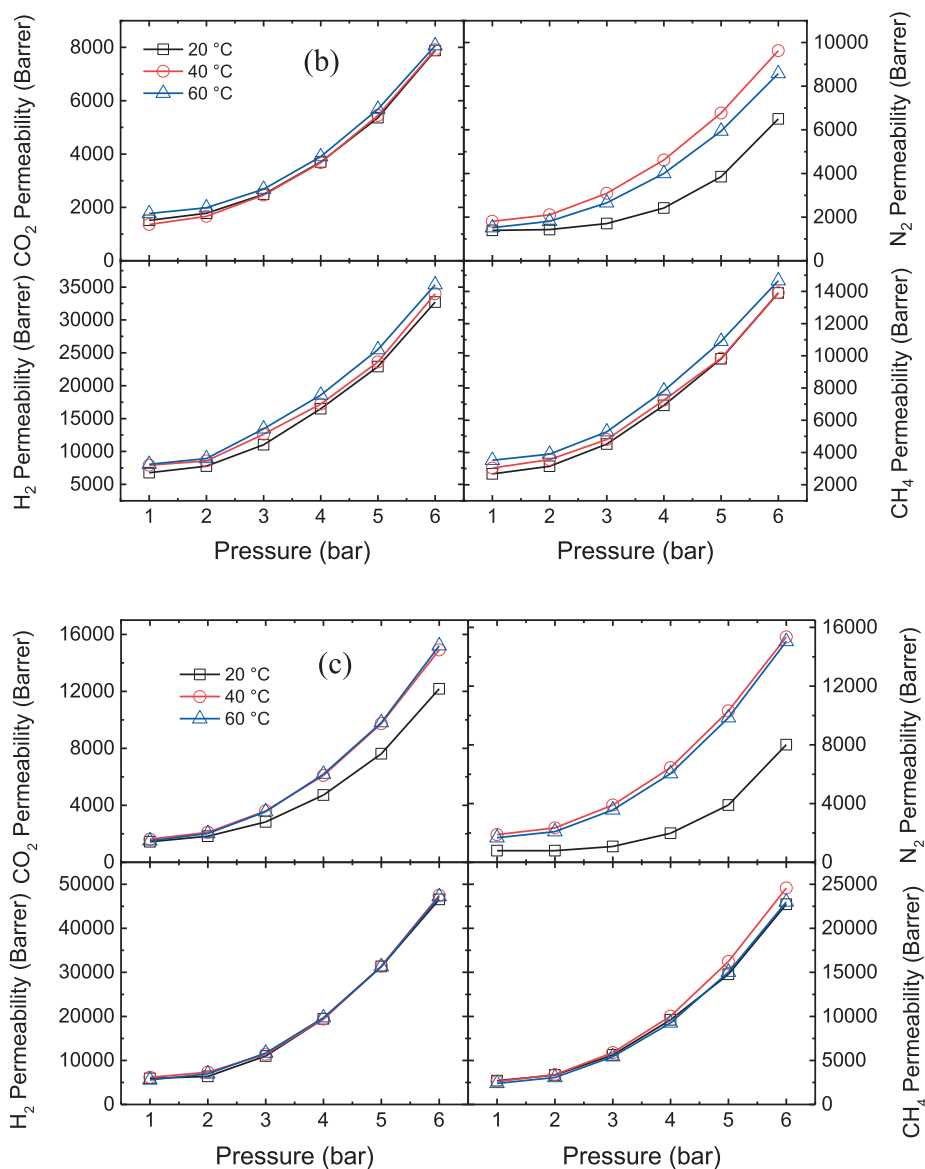


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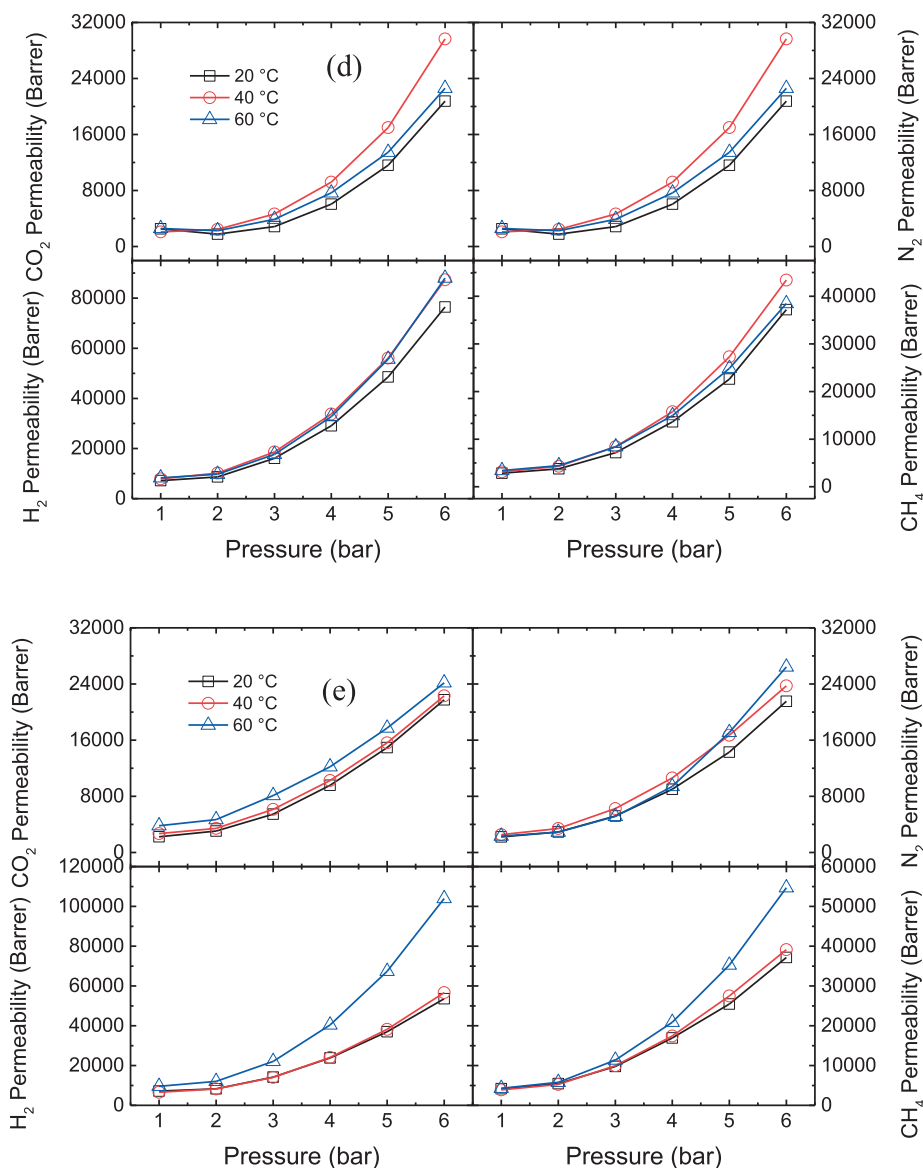


Fig. 5 (continued)

conducted by TGA analysis as shown in Fig. 3b. It can be observed that the thermal decomposition curve of all samples begins from 375 to 580 °C with a weight loss of 65 wt% due to the composition of the polymer (Yousef et al., 2021). There is no weight loss up to 100° C for all the preparations membranes; confirm the evaporation of the remaining solvent in the membranes. According to the results, adding GNs to the PES matrix did not show significant improvement in the membrane thermal stability. The beginning degradation temperatures of pristine PES and MMMs were similar and the degradation temperature of MMMs was not considerably changed when GNs was added (2 wt%) (Farnam et al., 2016).

3.1. Evaluation of gas permeability

Pure gas permeation experiments were carried out using pure CO₂, N₂, H₂ and CH₄ gases at various pressures of 1, 2, 3, 4, 5 and 6 bar to investigate the efficiency of membrane gas

separation. From the preliminary results, it appears that the maximum membrane capacity to withstand the transmembrane pressure and temperature are 8 bar and 70 °C without deteriorating membrane properties. Based on that, the main experiments were performed up to 6 bar and 60 °C. Fig. 4 shows the CO₂, N₂, H₂ and CH₄ permeability of all the prepared mixed matrix membranes at 20 °C. It was observed that by increasing the pressure from 1 to 6 bar, the permeability of CO₂, N₂, H₂ and CH₄ are increased. The permeability of CO₂, N₂, H₂ and CH₄ for the PES-GNs4 increases from 2246 to 21739, 2235 to 21535, 7151 to 53589, and 4176 to 37,159 Barrer, respectively with increasing the pressure. In addition, the CO₂, N₂, H₂ and CH₄ permeability of the PES increases from 9 to 13, 11–14, 9–12, and 3–5 Barrer by increasing the pressure. This behaviour attributed to the increased driving force for the transport of gas via membranes. As the pressure increases, the macromolecular segments are displaced close to each other. Therefore, the inter-segmental void space decreases, the

selective layer area increases and the density of the polymer increases, which leads to the increase of permeability (Farnam et al., 2016; Azizi et al., 2019; Alsari et al., 2007).

Moreover, H₂ and CH₄ have the maximum permeability more than CO₂ and N₂. This is due to the affinity and the larger diffusivity of H₂ and CH₄ molecules to the MMMs are greater than that of CO₂ and N₂ (Alkhouzaam et al., 2016; Wang et al., 2015). In addition, it was noticed that by increasing the loading of GNs from 0.01 and 0.04 wt%, the gas permeability was further enhanced. The permeability of CO₂, N₂, H₂ and CH₄ for the PES-GNs4 increases from 9 to 2246, 11 to 2235, 9 to 7151, and 3 to 4176 Barrer, respectively as compared with pure PES membrane at 1 bar. This is due to the presence of GNs assisting the absorption of gasses in the polymer and the increases of the porosity that offers more channels for the gas, resulting in higher permeation through the membrane (Luque-Alled et al., 2020; Kamble et al., 2020). Therefore, the combination of PES and GNs into the polymer matrix enhanced the membrane permeability and separation performance. PES-GNs4 showed the highest permeability for all the gasses among the synthesized MMMs at all the feed pressure.

The effects of different temperatures on the permeability of CO₂, N₂, H₂ and CH₄ gases for the prepared membranes at various pressures have been shown in Fig. 5a, b, c, d and e. The result shows that by increasing the temperature from 20 to 60 °C, the permeability of CO₂, N₂, H₂ and CH₄ gases through prepared membranes improves due to the enhancement of polymer chain movements and the presence of plasticization in the membranes (Zia-ul-Mustafa et al., 2019; Lasseguette et al., 2018). For pristine PES membrane, the permeability of CO₂, N₂, H₂ and CH₄ increases from 12.5 to 14.2, 14.2 to 16.1, 11.8 to 12.1, and 5 to 5.4 Barrer respectively at 6 bar. Whereas, at PES-GNs4, the permeability of CO₂, N₂, H₂ and CH₄ increases from 21,740 to 24171.5, 21534.7 to 26425.3, 53589.1 to 103951.6, 37159.6 to 54678.2 Barrer respectively at 6 bar. This means that the permeability of CO₂, N₂, H₂ and CH₄ for PES and PES-GNs4 increased about 13.6, 13.4, 2.6, 8 % and 11.2, 22.7, 94, 47.1% respectively when the temperature raised from 20 to 60 °C.

3.2. Evaluation of gas selectivity

Selectivity illustrates how well a polymeric membrane can separate the two gases from each other and is known as the permeability ratio of pure gas components (P_A/P_B) (Alkhouzaam et al., 2016). Fig. 6 shows the CO₂/N₂, CO₂/H₂ and CO₂/CH₄ selectivity at different pressure (1–6 bar) and 20 °C. The result shows that by increasing the pressure, the selectivity decreased slightly. For PES membrane, the H₂/CO₂, H₂/N₂ and H₂/CH₄ selectivity decreased from 0.97 to 0.94, 0.81 to 0.83 and 2.5 to 2.4, respectively, with the decreasing rates of 3, 2 and 4 %. In addition, the H₂/CO₂, H₂/N₂ and H₂/CH₄ selectivity for the PES-GNs4 membrane is decreased by increasing the pressure from 1 to 6 bar about 22, 22 and 18 % respectively at 20 °C. Meanwhile, the selectivity of H₂/N₂ for the PES-GNs2 membrane is decreased by increasing the pressure by about 23 %. It can be observed that for all the prepared membranes, H₂/N₂ exhibited the highest gas selectivity and H₂/CH₄ has the lowest selectivity due to the gas diffusion and solubility

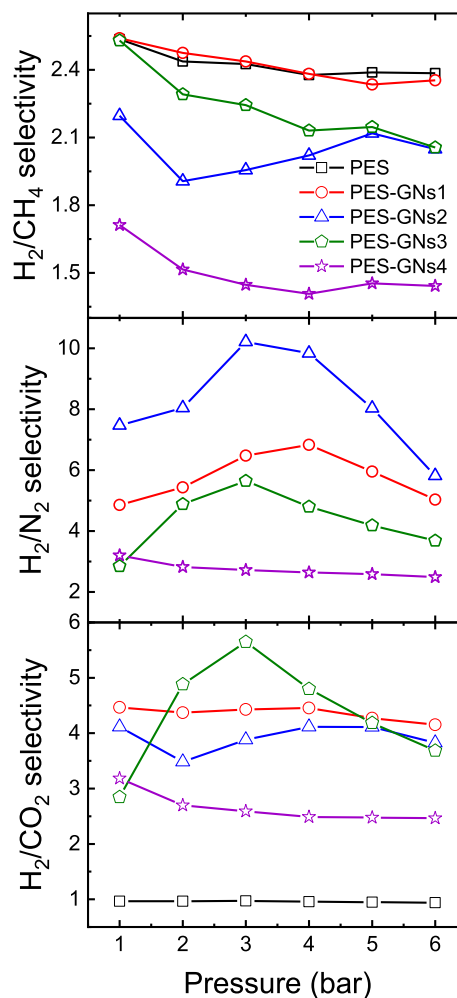


Fig. 6 H₂/CO₂, H₂/N₂ and H₂/CH₄ Selectivity behavior with different pressure at 20 °C.

mechanism (Lasseguette et al., 2018). The maximum selectivity of the H₂/N₂ gas obtained via the PES-GNs2 membrane is 7.5 without a decrease in the permeability. This behaviour is due to the properties of PES, which is considered a strong H₂ adsorbent that facilitated the H₂ permeability over N₂ gas through the membrane (Yousef et al., 2021; Akhmetshina et al., 2019).

MMMs are a viable alternative to regular polymeric membranes because they can eliminate the “trade-off” impact that plagues commercial membranes. Several aspects influence the effectiveness of MMMs in CO₂ separation procedures, including filler type and physicochemical qualities, nature of a polymer matrix, filler-matrix interaction, processing techniques, and so on. One of the most important aspects of developing effective MMMs is the choice of filler material. The selection of an adequate filler is difficult because filler materials may have poor adherence in the polymer matrix, resulting in poor CO₂ separation performance (Rodenas et al., 2015). Table 1 displays recent developments in the fabrication of MMMs using different filler exhibiting unique textural and surface properties such as MWCNTs, GO, GNs, and MIL-53.

Table 1 Comparison of PES gas permeation properties.

Materials	Parameter		Permeability (Barrer)				Selectivity	Ref
	Pressure (Bar)	Temperature (°C)	CO ₂	N ₂	H ₂	CH ₄		
PES	2	25	3			0.24	12.83	(Zia-ul-Mustafa et al., 2019)
PES		22	3675.4 GPU	3118.1 GPU			1.2	(Wang et al., 2015)
PDMS/seed/PES		22	810.1 GPU	52.4 GPU			15.5	(Wang et al., 2015)
PES	2	25	55 GPU			11 GPU	5	(Farnam et al., 2016)
PES + 20wt.%PVA	2	25	119 GPU			7	17	(Farnam et al., 2016)
PES/MWCNTs	4		2.99 GPU	1.5 GPU		0.75 GPU	2, 4	(Ismail et al., 2011)
GO/PES	1	30	662 GPU			18 GPU	36,	(Wang et al., 2016)
GO/PES	1	25	8500	425			20	(Kim et al., 2013)
PES/A-MIL-53 (Al)	5		4.5 GPU			0.08 GPU	54	(Ahmadijokani et al., 2019)
PES	2	20	10	12	10	4	1, 0.8, 2.5	Present study
PES-GNs1	2	20	1780	1432	7780	3143	4.4, 5.4, 2.5	Present study
PES-GNs2	2	20	1828	792	6367	3339	3.5, 8, 1.9	Present study
PES-GNs3	2	20	1775	1775	8667	3782	4.9, 4.9, 2.3	Present study
PES-GNs4	2	20	3067	2934	8275	5462	2.7, 2.8, 1.5	Present study

4. Conclusions

In this work, GNs with different loading were successfully embedded into PES for preparing mixed matrix membranes by a phase inversion process that has excellent separation and selectivity for gases. The prepared MMMs exhibited high mechanical stability, hydrophilicity and permeability. SEM results showed that the MMMs are smooth and homogeneous surfaces with a uniform structure consisting of a thin dense and porous layer. The TGA results showed that the thermal stability of the MMMs didn't change significantly in comparison to the PES membrane. The prepared MMMs have the capacity to operate without thermal degeneration and plasticization under high pressure of up to 6 bar and high temperature of up to 60 °C. The gas separation and selectivity have been increased with increasing the GNs loading, resulting in the formation of nanofiltration membrane. By increasing the GNs loading from 0 to 0.04 wt%, the permeability of CO₂, N₂, H₂, and CH₄ increased about 24856, 20218, 79,356 and 139,100 % respectively at 1 bar and 20 °C due to improving the membrane absorption and porosity. The result demonstrated that by increasing the pressure, the permeability of CO₂, N₂, H₂, and CH₄ have also increased. In addition, the selectivity of CO₂/N₂, CO₂/H₂, and CO₂/CH₄ increased by increasing the pressure and the GNs loading. CO₂/N₂ exhibited the highest gas selectivity and CO₂/H₂ has the lowest selectivity for all the MMMs. Consequently, the prepared membranes exhibited higher gas separation and selectivity as well as better mechanical properties compared to the pure PES membrane. Finally, the synthesized membrane achieved improved gas separation performance, which significantly contribute to post-combustion carbon capture and storage in the industry, lowering CO₂ emissions and reducing climate change risk.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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