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The Effect of Multi-Walled Carbon Nanotubes on CO_2/N_2 Separation Using Sulfonated Polyether Ether Ketone/Polyetherimide Nano Composite Membrane

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ABSTRACT

Membrane technology has attracted significant research attention due to its many advantages in gas separation. In the present study, Blended membranes were fabricated utilizing sulfonated poly (ether ether ketone) (SPEEK) and poly (etherimide) (PEI) with varying quantities of multi-wall carbon nanotubes (MWCNTs) (up to 2 wt.%). The membranes produced were analyzed using X-ray diffraction (XRD), scanning field emission electron microscopy (FESEM), and Fourier transformed infrared spectroscopy (FTIR). The impact of the SPEEK/PEI composition on membrane selectivity was examined at various feed pressures ranging from 2 to 8 bar. The selectivity and gas permeability values varied between the individual polymers and showed systematic fluctuations with changes in the SPEEK/PEI content in the blends. The incorporation of MWCNTs into the blend resulted in an enhancement of the CO_2/ N_2 selectivity. The membrane containing the same amount of SPEEK and PEI, along with 1 wt.% of MWCNTs (designated as SP55M1), exhibited an approximately 22% increase in the selectivity of CO_2/N_2 compared to the pristine membrane.

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1. Introduction:

The emission of CO_2 due to the growth of fossil fuel power plants and energy industries is unavoidable. Excessive CO_2 emissions have significantly contributed to global warming, rising sea levels, and climate change. Therefore, the conversion, capture, and separation of CO_2 are of paramount importance in addressing the environmental challenges that have garnered substantial attention in science and engineering [1, 2]. Several conventional techniques such as amine absorption, pressure swing adsorption (PSA), and cryogenic distillation are employed for CO_2 separation [3]. However, these processes entail high energy and cost expenditures. Membrane technology offers an energy-efficient solution for CO_2 separation [4, 5]. The features of membrane processes, such as simplicity, minimum residual effect, and cost-effectiveness, make them competitive with conventional gas separation processes [6]. Membrane technology has been repeatedly used for gas mixture separation in the petroleum, gas, and petrochemical industries. Gas separation through membranes occurs without a phase change, resulting in cost reduction [7]. Remarkable progress has been made in the past two decades in improving the performance of polymer membranes for gas separation [8]. One of the methods for improving the membrane properties is the incorporation of nanomaterials into the polymer matrix. Due to their small size and high surface area, membranes made from these materials not only exhibit the ability to interact effectively with the separating gas and, thus high selectivity but also possess desirable mechanical and thermal resistance [9]. The most commonly investigated polymers for gas separation are polyetherimide (PEI) and poly (ether ketone) (PEEK) [10]. PEEK is a promising polymer with gas separation properties [11]. It has been reported that sulfonic groups in membrane materials are effective in enhancing membrane separation performance [12]. PEI and SPEEK, like other polymers, face a trade-off between selectivity and permeability. To address this issue, fillers should be added during membrane preparation to form mixed matrix membranes (MMMs). Such fillers create voids within the polymer, improving gas transport [5, 13]. Various non-porous fillers, such as SiO_2 [14], metal oxides [15], alumina [6], clay [16], and porous zeolite fillers [17, 18], as well as carbon molecular sieves [19], and multi-walled carbon nanotubes (MWCNTs) [20], have been tested. Among these, MWCNTs have garnered significant research interest due to their excellent mechanical properties and porous structure [21, 22]. When MWCNTs are incorporated into the polymer matrix, strong interactions between polymer chains and MWCNTs can strengthen the polymer structure and significantly improve gas permeation behavior [23].

In this research, composite membranes for gas separation were created using multi-walled carbon nanotubes (MWCNTs) as fillers, and polyetherimide (PEI) and sulfonated polyether ether ketone (SPEEK) as polymer matrices. The prepared composite membranes were thoroughly examined through analyses to assess their structural properties. The influence of polymer blending on the membrane's separation performance was studied. The results demonstrated that composite membranes exhibited better separation performance compared to pure membranes, especially when separating CO_2 from N_2 gas.

2. Materials and Methods

Polyether ether ketone with a molecular weight of 20,800 and polyetherimide with a molecular weight of 35,000 were obtained from Sigma-Aldrich. 1-Methyl-2-pyrrolidone, sulfuric acid, and nitric acid were obtained from Merck, Germany. Multi-walled carbon nanotubes were obtained from the US-Nano company.

2.1. Functionalization of Multi-Walled Carbon Nanotubes

In order to improve the dispersion of MWCNT to the solvent (NMP), was first functionalized the nanotube with COOH group. An amount of MWCNTs (0.5 gr) were mixed with a volume ratio of 3:1 of nitric acid and sulfuric acid. They were then placed in an ultrasonic bath at a temperature of 50°C for one hour and then refluxed at room temperature for 24 hours. The resulting solution was washed with distilled water until it reached a pH of 7. The product was dried in a vacuum oven at 75°C [21-23].

2.2. Sulfonation of Polyether Ether Ketone (SPEEK)

Sulfonated polyether ether ketone (SPEEK) was prepared using the sulfonation method [24-26]. 4.5 gr of dry SPEEK polymer was gradually added to 100 ml of 98% volume sulfuric acid. The mixture was vigorously stirred at 30°C for 16 hours. After complete dissolution, the mixture was slowly added to ice-cold water while stirring vigorously, and the milky white precipitate was formed. The formed precipitate was washed twice with distilled water until its pH became neutral. The synthesized SPEEK was then dried in a dry environment for a week and subsequently placed in a vacuum oven at 60°C for 24 hours to remove any remaining solvent. The degree of sulfonation was determined to be 72% by titration [27].

2.3. Preparation of Polymer Membranes

SPEEK/PEI nanocomposite membranes were prepared using the thermal phase separation method (solvent evaporation). At first, SPEEK and PEI were dried in a vacuum oven at 80°C for 6 hours to remove moisture. Polymer solutions were prepared by dissolving 3% w/w (0.3 gr) of SPEEK or PEI in 10 mL of NMP at 60°C for 8 hours. The prepared solutions were cast onto Teflon sheets and dried following a thermal schedule. Initially, they were held at 50°C for 5 hours, then the temperature was increased to 70°C and maintained for 4 hours, and finally, the temperature was raised to 90°C and held for an additional 3 hours. The resulting films were separated from the Teflon sheets and placed in a vacuum oven at 70°C for 5 hours to remove any remaining solvent.

2.4. Modification of SPEEK/PEI Composite Membranes

To prepare nanocomposite membranes, multi-walled carbon nanotubes (MWCNTs) were first dispersed in 1-methyl-2-pyrrolidone solvent at weight percentages of 0.5%, 1%, and 2%. The dispersion was placed in an ultrasonic homogenizer for 3 hours to ensure uniform dispersion of MWCNTs in the solvent. The resulting solution was placed on a magnetic hitter at a temperature of 55°C. Then, a specific weight percentage of SPEEK was added to the solution, and continuous stirring was carried out for 6 hours. Furthermore, PEI was added to the solution at the same temperature and stirred for 6 hours. To prevent bubble formation, stirring was paused for 30 minutes. Finally, the mixture was cast into Teflon containers, and membranes were formed following the thermal schedule mentioned earlier. The prepared membranes had thicknesses ranging from 40 to 60 microns, which were measured using a micrometer. The membranes were labeled according to the polymer and MWCNT loading (Table 1).

Table 1. Synthesized membranes according to the Taguchi experimental method

Sample code	speech (wt.%)	PEI (wt.%)	MWCNTs (wt.%)	Pressure (bar)
sPEEK	100	0	0	2
S3M0.5	100	0	0.5	4
S3M1	100	0	1	6
S3M2	100	0	2	8
SP82	80	20	0	4
SP82M0.5	80	20	0.5	2
SP82M1	80	20	1	8
SP82M2	80	20	2	6
SP55	50	50	0	6
SP55M0.5	50	50	0.5	8
SP55M1	50	50	1	2
SP55M2	50	50	2	4
SP28	20	80	0	8
SP28M0.5	20	80	0.5	6
SP28M1	20	80	1	4
SP28M2	20	80	2	2
PEI	0	100	0	2
P3M0.5	0	100	0.5	4
P3M1	0	100	1	6
P3M2	0	100	2	8

2.5. Characterization Tests

Field-emission scanning electron microscopy (FE-SEM) using a MARIA model FE-SEM microscope, TE-SCAN (Czech) was employed to examine the surface morphology and distribution of carbon nanotubes in the membranes. Fourier-transform infrared spectroscopy (FTIR) was used to investigate the structure of the prepared membranes. The membranes were analyzed using a JASCO FTIR-6300 FTIR spectrometer (Japan). The analysis was conducted in the range of 400 cm^{-1} to 4000 cm^{-1}. In order to investigate the crystallinity and potential structural changes in the polymer matrix, the X-ray diffraction (XRD) model PW1730, Philips (Netherlands) was employed.

2.6. Measurement of Gas Permeability in Membranes

After the preparation of composite membranes using SPEEK and PEI, as well as composite membranes of polymer/multi-walled carbon nanotubes (MWCNTs), these membranes were subjected to gas permeability testing for nitrogen and carbon dioxide gases. The time lag method was employed to investigate gas permeability. The time lag method is the most common technique for gas permeability testing in polymer membranes [28]. In this method, gas permeation through the polymer is measured and analyzed from the initial time until the polymer's permeability reaches a constant value. To assess the amount of permeated gas through the membrane and record the gas flow rate, the constant pressure method was used. In the constant pressure method, the pressure on the feed side is low, and variations in the gas volume that passes through the membrane are recorded. Fig. 1 illustrates the overall diagram of the gas permeability measurement apparatus. By changing the input gas pressure within the range of 2 to 8 bar and at a temperature of 30 °C, the permeability coefficients were calculated using equation (1):

$$P = \frac{Q \times L}{\Delta P \times A} \qquad (1)$$

In this equation (1Barrer $=10^{-10}$($cm^3 cm/cm^2.s. cmHg$)), P represents gas permeability, Q is the flow rate of the gas (calculated as the slope of the volume-time curve), L is the thickness of the membrane (in cm), ΔP is the pressure difference across the membrane (in cmHg), and A is the effective surface area of the membrane (in cm^2). The ideal selectivity related to the permeability of pure carbon dioxide (CO_2) and nitrogen (N_2) gases was calculated as equation (2) [29]:

$$\alpha_{CO_2/N_2} = \frac{P_{CO_2}}{P_{N_2}} \qquad (2)$$

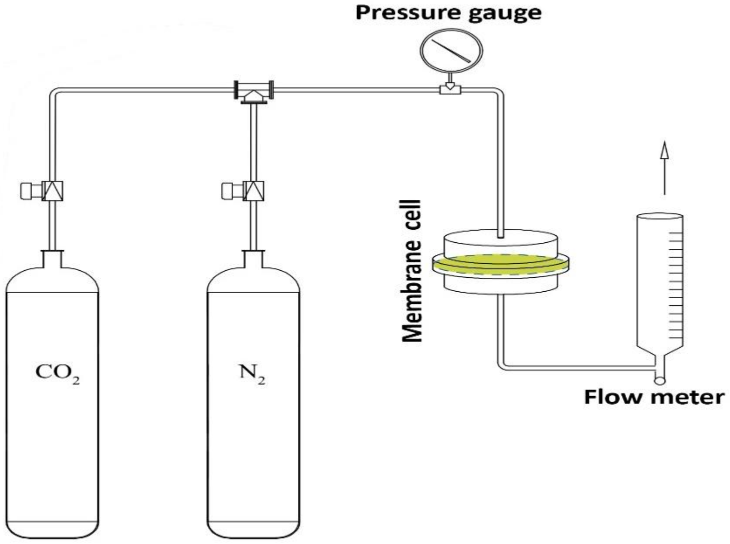

Fig. 1. Schematic diagram of the gas permeability measurement apparatus.

3. Results and Discussion

3.1. Fourier-Transform Infrared (FTIR) Analysis

The FTIR spectrum of functionalized multi-wall carbon nanotubes (MWCNTs) with carboxyl groups before and after modification is shown in Fig. 2. In this spectrum, the stretching vibrations of OH groups at 3440 cm^{-1} were observed as a broad absorption peak. The peak at 1580 cm^{-1} can be attributed to the C=C bond in MWCNTs. The peak at 1160 cm^{-1} was assigned to the C-C bond. Additionally, the characteristic carboxyl peaks were observed at 1650 cm^{-1} and 1720 cm^{-1} [30].

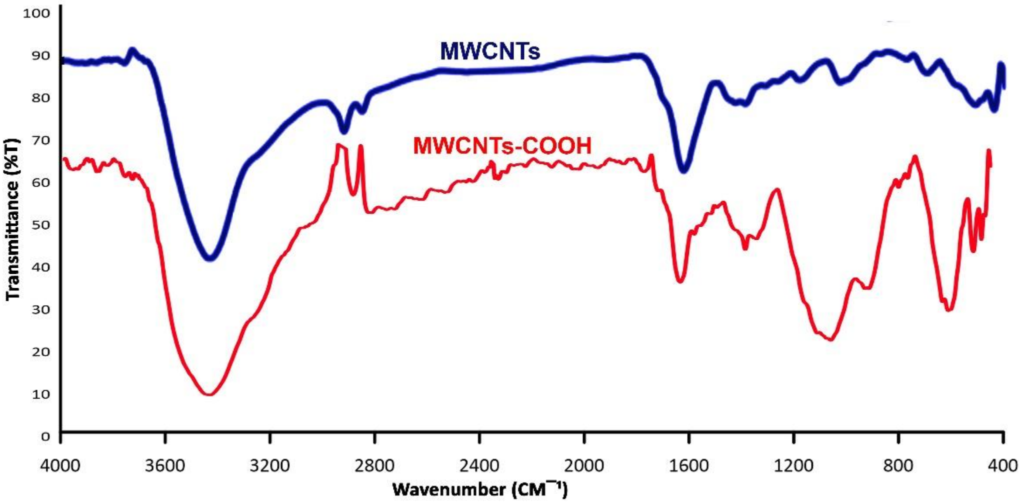

Fig. 2. FTIR spectra typical of MWCNTs and MWCNTs-COOH

The FTIR spectra of PEI and SPEEK membranes were analyzed to study their structures, as shown in Fig. 3. The broad band observed at 3400 cm^{-1} in the SPEEK membrane may be attributed to the OH vibration of the sulfonic acid groups which interacted with the water molecular. Additionally, in the SPEEK membrane, symmetric and asymmetric sulfonic acid groups' stretching vibration peaks were seen at 1020 cm^{-1} and 1220 cm^{-1}, respectively [31-34]. According to the spectra of the characteristic PEI membrane, absorption peaks are as flowing: imide group 1716 cm^{-1} and 1775 cm^{-1} corresponding to symmetric and asymmetric stretching of carbonyl imide group, CN bending and stretching 737 cm^{-1} and 1348 cm^{-1} respectively, aromatic carbon C = C 1595, aromatic ether (C-O-C) 1232 cm^{-1} [35, 36].

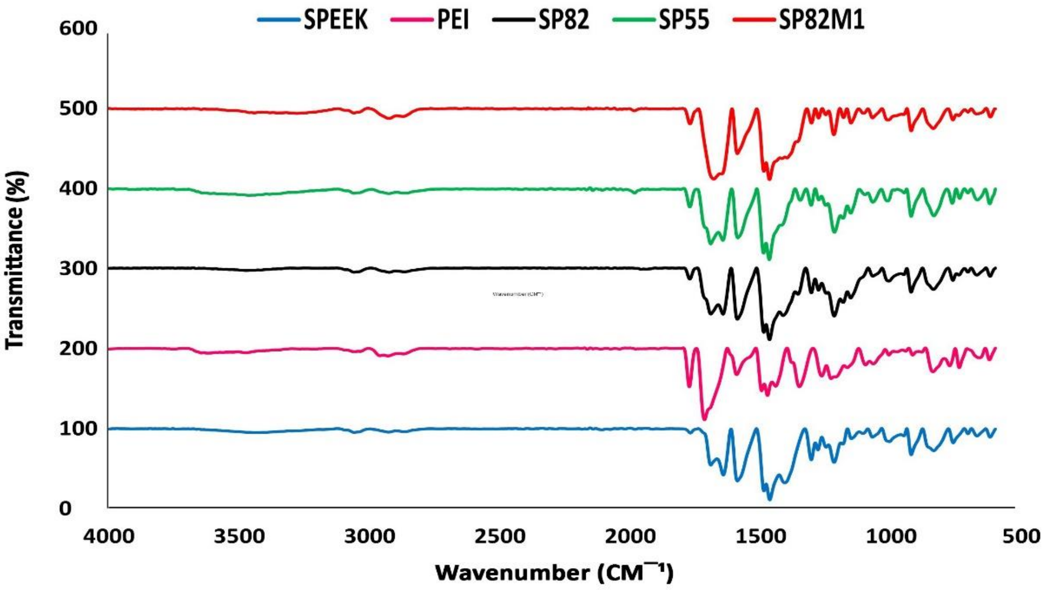

Fig. 3. FTIR spectra of the neat and mixed matrix membranes.

The addition of MWCNTs to the nanocomposite membranes revealed a new absorption peak at 1717 cm^{-1}, attributed to the carbonyl tensile of carboxylic acid groups in MWCNTs. Therefore, the amino and sulfonic acid groups have bonded to MWCNT-COOH after reacting with SPEEK and PEI. Similar results from FTIR spectra have been reported for various types of MWCNTs in other studies [37, 38]. The functionalization of carbon nanotubes with these active groups offers several advantages, including creating a uniform environment and promoting effective dispersion of MWCNTs within the polymer matrix. Additionally, these functional groups activate the surfaces of MWCNTs by forming new bonds, such as carboxylic acid or hydroxyl groups.

3.2. X-ray Diffraction Analysis

The spectrum of MWCNT-COOH is presented in Fig. 4. The prominent peak observed at 26° corresponds to the hexagonal graphite (002) C, which is identifiable [39]. The peak sharpness at an angle of 26° indicates that the structure of MWCNTs remains unoxidized. This is because any reduction in crystallinity order in MWCNTs would result in broader XRD peaks and a shift of the diffraction peak towards lower angles. Additional distinct peaks of crystalline graphite are observed at approximately 43°, 53° and 77°, corresponding to the XRD peaks of C (100), C (004), and C (110) graphite, respectively. The crystallite size was determined from the full width at half maximum (FWHM) of the diffraction peaks using the Scherrer relationship. The following values were obtained: D = 162 A for MWCNT and 79 A for MWCNT-COOH. The diffraction peak selected to determine the crystallite size was 26°, which corresponded to the crystal plane (002). This means that the size of the crystallites corresponds to the length of the MWCNTs [40].

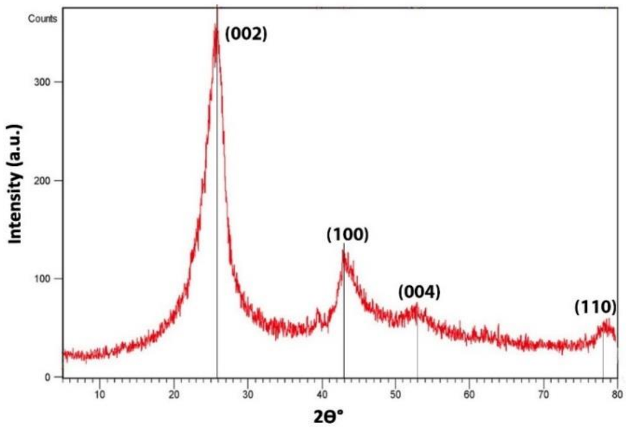

Fig. 4. X-ray Diffraction of MWCNT-COOH

Sharp peaks in XRD data indicate crystalline regions, while broad peaks represent amorphous or disordered regions. XRD spectra of pure, composite, and nanocomposite membranes are presented in Fig. 5. Pure SPEEK and PEI membranes show a diffraction peak at 18.71 degrees, associated with crystalline regions in the pure polymers, as these polymers are semi-crystalline. The remaining peaks are attributed to the remaining amorphous regions. As observed in Fig. 5, the combination of SPEEK and PEI causes the sharp peaks to shift to 18.68°. These stronger peaks indicate significant molecular interactions between the polymers. Furthermore, combining the polymers at different ratios results in a slightly lower 2.4-degree crystallinity change compared to that in pure polymers. The cause for such a shift is the change in the lattice unit cell volume due to the difference in ionic radii between the host lattice ion and the dopant ion. A bigger dopant ion will result in an increase in the unit cell volume, and a smaller dopant ion will result in a decrease in the unit cell volume. This modification of composite membranes leads to greater miscibility, which, in turn, enhances permeability compared to pure polymers. When 1% MWCNT is added to the polymer blend (SP82M1), a distinct peak at 26° is observed, indicating the presence of carbon nanotubes. Adding carbon nanotubes to the membranes can improve gas permeability and selectivity by increasing crystallinity up to 1% [41-43].

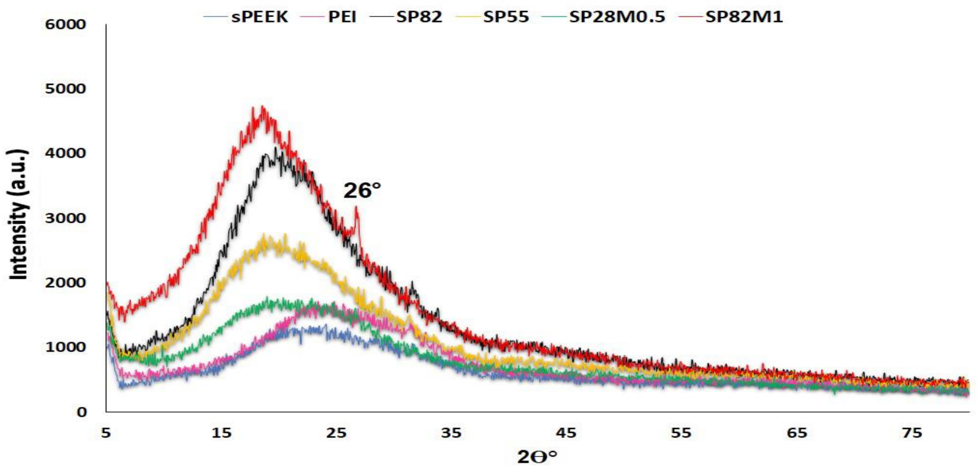

Fig. 5. X-ray Diffraction of Nanocomposite Membranes

3.3. Field Emission Scanning Electron Microscopy (FESEM) Analysis

Fig. 6a,b depicts cross-sectional images of pure SPEEK and PEI membranes. A thin and dense layer of pure membranes is observable. Fig. 6c shows cross-sectional images of SP82 membranes. As shown in Fig. 6d, MWCNTs were likely uniformly dispersed in the polymer matrix (1 wt.%) without agglomeration. Moreover, pure membranes have a completely uniform structure, while in the nanocomposite membranes (as shown in Fig. 6d), due to weak Van der Waals interactions between carbon nanotubes and the polymer structure, carbon nanotubes are well dispersed without clustering, and due to the presence of amorphous chains in the polymer, carbon nanotubes are well surrounded by the polymer without defects [44]. In order to confirm the compatibility of MWCNTs, studies on the gas permeability of CO_2 and N_2 for various membrane types were conducted. Due to the high solubility of carbon dioxide alongside its small kinetic diameter, it exhibits the property of softening the membrane and separating polymer chains from each other. Figures 7 and 8 show the permeability values for SP82 and SP82M1.

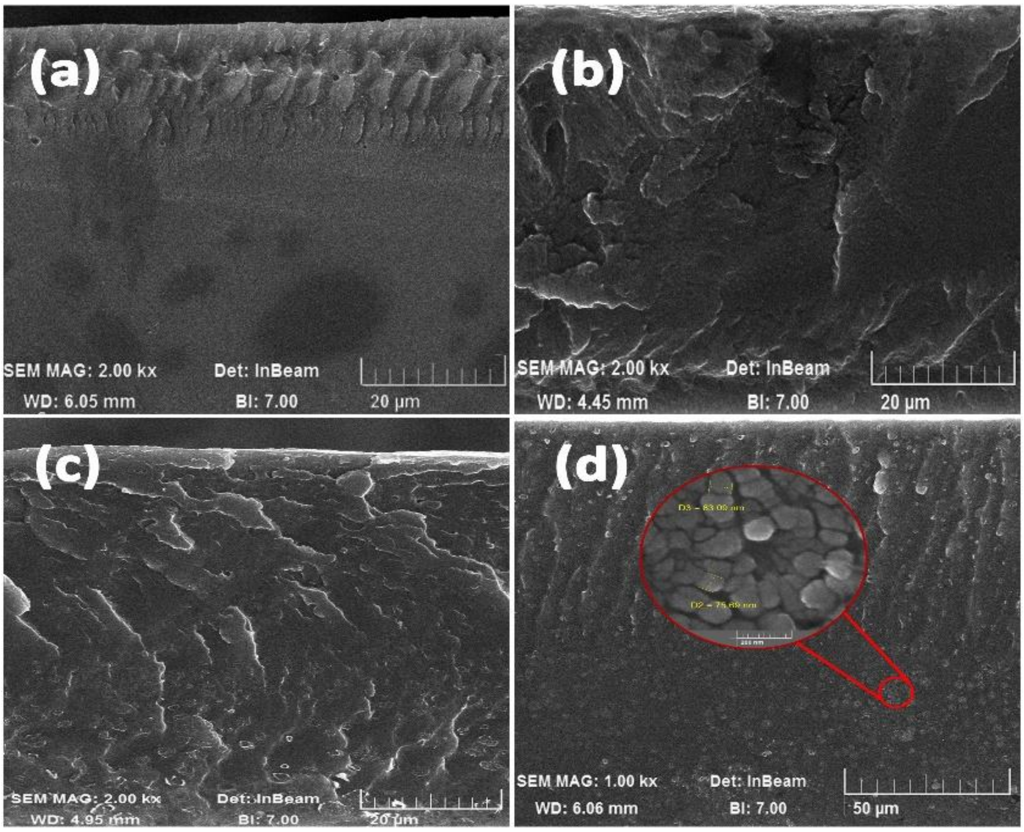

Fig. 6. FESEM cross-sectional images of composite membranes: (a) PEI, (b) SPEEK, (c) SP82, and (d) SP82M1.

3.4. Gas Transport and Selectivity Properties

Gas permeability of CO_2 and N_2 was measured using the constant-pressure, variable-volume method at a temperature of 30° C and pressures of 2, 4, 6, and 8 bars for all fabricated membranes. As observed in the graphs, there is a significant difference in gas permeability between CO_2 and N_2. This difference is due to the high solubility of carbon dioxide, which, along with its small kinetic diameter, causes the membrane to soften and separate polymer chains. On the other hand, glassy polymers perform gas separation based on molecular size, and the solubility of gas is the determining factor in the dissolution-permeation process. Therefore, the high solubility of carbon dioxide has resulted in increased permeability compared to nitrogen. Moreover, considering the 10-nanometer diameter of MWCNTs and their structure, it can be said that the cylindrical inner surface of MWCNTs adsorbs CO_2 molecules through surface diffusion, unlike N_2, which has weak interaction with MWCNTs and is scarcely adsorbed. Consequently, the nanotube channels provide an additional pathway for CO_2 transport. For SP55 and SP82 membranes, surface amine groups act as facilitated transport sites, aiding in the rapid and continuous transfer of CO_2 into the polymer matrix. Fig. 7b illustrates the permeability of membranes with 0.5% and 1% weight loading of MWCNTs, which is greater than membranes with loading above 2% weight. Some MWCNT agglomerates can reduce the free volume and increase MWCNT entanglement, leading to partial deterioration in permeation.

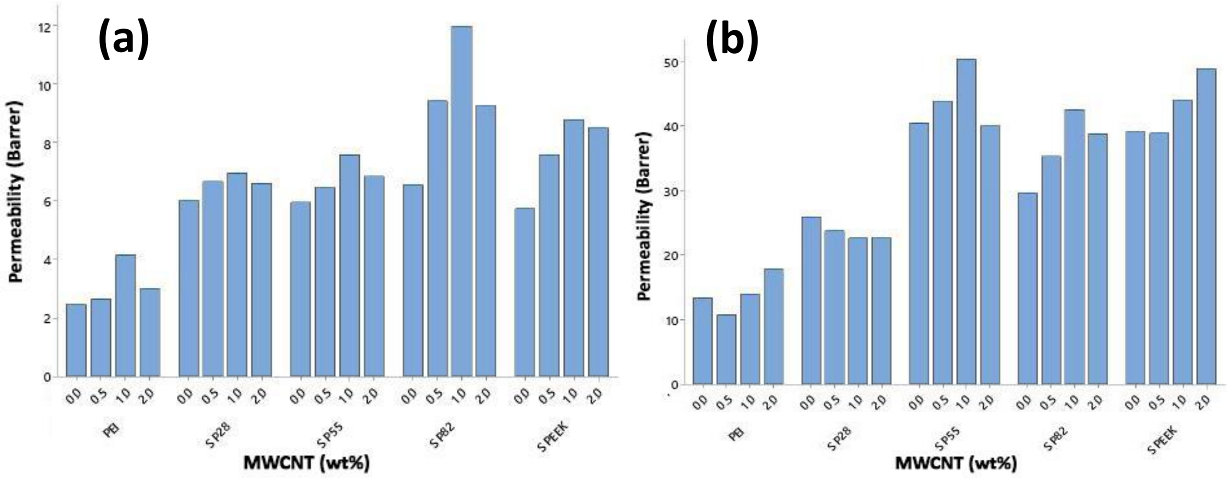

Fig. 7. MWCNTs' effect on (a) CH_4 and (b) CO_2 permeability in different mixed matrix membranes.

The impact of the addition of MWCNTs on the permeability of N_2 and CO_2 gases in various prepared membranes is illustrated in Figure 7a. It is evident from Fig. 7a that the permeability of CO_2 molecules was higher than that of N_2 molecules in all prepared membranes. This higher permeability of CO_2 molecules can be attributed to its larger condensation capacity and the quadrupole-dipole interaction between functional groups in the blend membranes and CO_2 molecules [45]. Additionally, the increased permeability of CO_2 gas with higher MWCNT content can be attributed to the sorption of CO_2 on MWCNTs due to the affinity between CO_2 gas and MWCNTs. It is important to note that in the case of functionalized MWCNTs, the presence of carboxyl groups led to greater interaction between the membrane and CO_2 molecules, ultimately resulting in increased CO_2 permeability through the membrane (see Fig. 8).

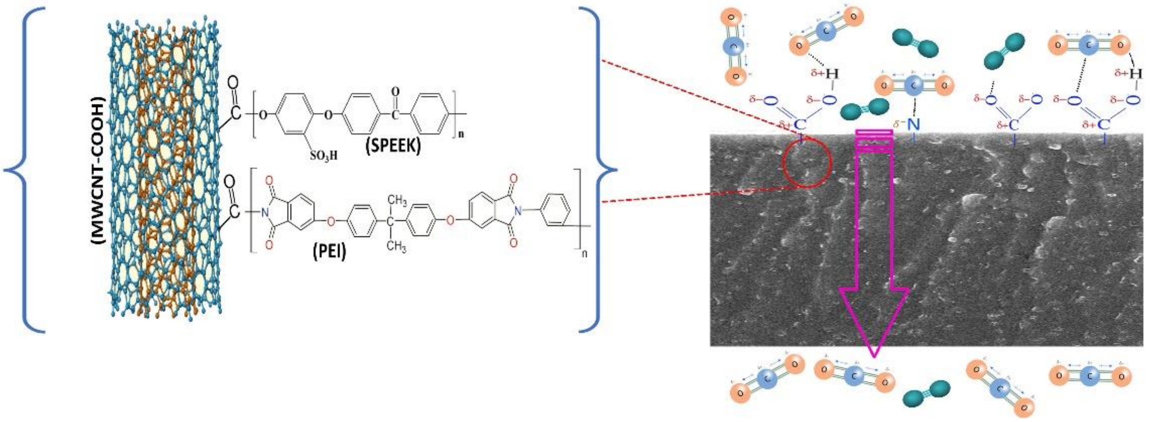

Fig. 8. Schematic of reactions between SPEEK/PEI/MWCNTs for membrane gas separation.

However, the permeability and selectivity of SP55M1 are significantly higher compared to other membranes and adding carbon nanotubes clearly improves permeability and selectivity. This improvement is attributed to microscopic voids in the membrane structure. Moreover, the use of functionalized COOH fillers in the polymer matrix greatly aids in compatibility and adhesion between the filler and polymer matrix [27]. The permeability and selectivity of the different MMMs are displayed in Table 2.

Table 2. Selectivity and permeability of pure polymer membranes and loaded MMMs.

Polymer	**Fillers**	**Loading (wt.%)**	**Permeability** CO_2 **(Barrer)**	**Permeability** N_2 **(Barrer)**	**Permeability** CO_2/N_2 **(Barrer)**	**Temperature and Pressure**	**Reference**
SPEEK/PEI (50/50)	MWCNTs	1	50.36	7.57	6.64	30 ºC, 2 bar	This work
SPEEK	MWCNTs	1	48.86	8.52	5.73	30 ºC, 8 bar	This work
PEI	MWCNTs	1	13.95	4.15	3.36	30 ºC, 6 bar	This work
SPEEK	-S-MIL-101(Cr)	20	35	0.85	41.1	30 ºC, 4 bar	[46]
SPEEK/PEI	TiO_2	15	21	0.91	22.9	25 ºC, 2 bar	[47]
Pebax	MWCNTs		174	4.1	42	45 ºC, 3.5 bar	[48]

Fig. 9 presents the selectivity of CO_2/N_2 for SPEEK/PEI/MWCNT membranes at 30°C. When compared to the unloaded membrane, the inclusion of MWCNT resulted in a significant increase in CO_2 permeability and a slight increase in CO_2/N_2 selectivity at high loads. The incorporation of filler into the membrane provided a substantial advantage, likely due to the presence of polar groups such as OH, which facilitated bonding between the MWCNT and CO_2 molecules. The highest selectivity is associated with the SP55 membrane with different loadings of MWCNTs.

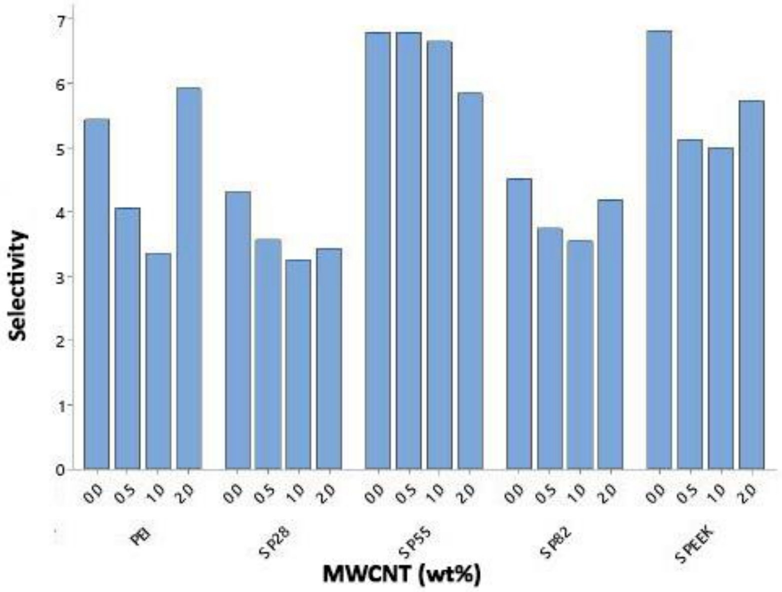

Fig. 9. CO_2/N_2 Gas Selectivity Diagram in SPEEK/PEI/MWCNT Membranes at 30°C

4. Conclusions

Membranes containing PEI and SPEEK polymers, and incorporated with MWCNTs were successfully prepared. The gas separation performance of the prepared membranes was investigated for CO_2 and N_2 gases. FESEM observations showed good dispersion of MWCNTs in SP82M1. The incorporation of modified MWCNTs into the polymer matrix resulted in improved CO_2/N_2 selectivity at 2 bars. The gas separation performance of the prepared membranes is strongly dependent on the properties of the permeating gas molecules and the pressure. Compared to the other researchers, the prepared nanocomposites were significantly efficient, which makes it a promising platform to use in related environmental processes.

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