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Preparation of a Poly (Ether-b-Amide) Mixed-Matrix Membrane and Its Application in Blast Furnace Gas

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Abstract: In this paper, we propose the use of nanomaterials to build three-dimensional structured gas-separation membranes to accommodate more gas molecules. SWCNT provides a fast passage for gas molecules, while GO can make gas molecules have more adsorption sites due to its large specific surface and the fact that its special lamellar folds can hinder the transport of macromolecules. Graphene oxide (GO) was prepared by an improved Hummer's method, and single-walled carbon nanotubes (SWCNTs) were purified by mixed acid treatment. Then, Pebax1657 particles were dissolved in a reflux setup at 80 °C, and GO/SWCNT/Pebax1657 mixed-matrix membrane (MMM) was prepared by solution blending. Finally, the permeability and selectivity of GO/SWCNT/Pebax1657 membrane to single gas and mixed gas at different temperature and inlet pressure were investigated.

Keywords: polyether amide; graphene oxide; carbon nanotubes; mixed matrix membrane; gas separation



Citation: Jiang, L.; Chen, Y.; Hou, X. Preparation of a Poly (Ether-b-Amide) Mixed-Matrix Membrane and Its Application in Blast Furnace Gas. *Coatings* **2022**, *12*, 1851. <https://doi.org/10.3390/coatings12121851>

Academic Editor: Stefan Ioan Voicu

Received: 17 October 2022

Accepted: 24 November 2022

Published: 29 November 2022

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1. Introduction

In the production processes of the metallurgical industry, the direct discharge of blast furnace gas produces a large amount of toxic gas that causes environmental pollution. The main incombustible components of blast furnace gas, such as CO₂, N₂, and CO, make direct cyclic utilization difficult. This increases the energy consumption of the metallurgical industry, which is not conducive to achieving the goals of energy consumption reduction and sustainable development. Therefore, there is an urgent need for a gas-separation technique to realize the separation, recovery, and utilization of CO₂, N₂, and CO [1]. In recent years, gas-separation membranes have gradually become the main methods of separating gases. Compared with traditional separation techniques, membrane separation has the advantages of low energy consumption, no phase change, and simple operation, so together they are regarded as one of the most promising gas-separation techniques. The membrane material is the core of the technique, as its characteristics directly determine the gas-separation efficiency and application prospects of the technique [2,3].

Membrane materials occupy an important position in membrane separation techniques, and various types of membrane materials have been fully developed such as polymer membranes that have the advantages of low manufacturing costs and easy processing but cannot surpass the Robeson upper bound [4]. Then there are inorganic membrane materials, which have relatively high permeability and selectivity, but they are relatively expensive and difficult to prepare, which limits their large-scale production. Mixed-matrix membranes (MMMs) with inorganic fillers as the dispersed phase and polymer matrix as the continuous phase have attracted the attention of researchers. The MMMs combine the advantages of polymer membranes and inorganic membranes and are thought to have great potential to surpass the Robeson upper bound, so selecting the appropriate dispersed phase and continuous phase has a crucial impact on improving the selectivity and permeability of the MMMs [5,6].

Poly(ether-b-amide) (Pebax) is prepared via the copolymerization of a polyether (PE) segment and a polyamide (PA) segment. PE provides good gas permeability and good affinity with CO₂ and other gases. PA represents the rigid segment of a saturated aliphatic chain PA, which has almost no permeability, but PA provides good mechanical properties [7,8]. As a commercialized block copolymer, Pebax1657 has good membrane-forming properties, excellent acid and alkali resistance, and high thermal and mechanical stability, but pure poly(ether-b-amide) membranes still cannot surpass the Robeson upper bound and easily aggregate. Therefore, it is necessary to dope other substances into the poly(ether-b-amide) to surpass the Robeson upper bound [9,10]. Azizi et al. [11] prepared Pebax/SiO₂, Pebax/TiO₂, and Pebax/Al₂O₃ membranes. Their permeabilities to CO₂ and CH₄ increased with increasing dopant content, and the permeability to CO₂ and the ideal selectivity for CO₂/CH₄ considerably increased with increasing pressure. Chen et al. [12] successfully synthesized the metal-organic framework material KAUST-7 with uniform particle size for the first time and mixed 6FDA-Durene polyimide into it to prepare a 6FDA/KAUST-7 membrane. It had good plasticization resistance and separation performance for CO₂/CH₄ and surpassed the Robeson upper bound. Dorosti et al. [13] used phase inversion to prepare Pebax/Fe-1,3,5-benzenetricarboxylate (BTC) membrane with Pebax1657 as the continuous phase and the metal-organic framework Fe-BTC as the dispersed phase. As the pressure increased to 7 Barrer, the permeability and selectivity for CO₂ and CH₄ gradually increased; under high pressure, the presence of doped particles restricted the migration and plasticization of the polymer chains. As a result, the permeability of CO₂ decreased, and the selectivity of CO₂/CH₄ increased first and then decreased; at a doping percentage of 40%, the permeability to CO₂ increased to 425.4 Barrer, and the selectivity for CO₂/CH₄ increased to 12.3. Isanejad et al. [14] used an amine functional group to modify SiO₂ nanoparticles, which were used as modifiers and added to Pebax polymer to prepare nanocomposite membranes. As the SiO₂ content increased, the permeability of the nanocomposite membrane first increased and then decreased. When the doping percentage was 15%, the permeability to CO₂ and the selectivity for CO₂/CH₄ increased by 10% and 14%, respectively. As the feed pressure increased, the selectivity for CO₂/CH₄ fluctuated, with a slight increase overall, reaching a maximum of 40.16. Estahbanati et al. [15] used ionic liquid and Pebax1657 polymer to prepare a new type of ionic liquid composite membrane. Due to the unique attractive force of this ionic liquid to CO₂, the permeability and selectivity of the composite membrane were greatly increased. The addition of ionic liquid led to a more amorphous structure of the polymer membrane and less crystallinity, resulting in increases in both CO₂ permeability and selectivity. Lee et al. [16] blended a graft copolymer (poly(2-[3-(2H-benzotriazol-2-yl)-4-hydroxyphenyl] ethyl (PBE) methacrylate)-graft-poly (oxyethylene methacrylate)) with Pebax to prepare an MMM, which gave rise to interconnected CO₂ network channels, thereby increasing the solubility of CO₂. With increasing content of PBE filler, gas permeability and selectivity gradually increased, and the permeability to CO₂ reached 224.4 Barrer; when the PBE content was 5%, the permeability to CO₂ was 175.3 Barrer, and the selectivity for CO₂/N₂ reached 48.2.

Different dopants have different effects on MMMs, so the choice of dopant has a critical influence on the performance of an MMM. In recent years, nanofillers, including carbon nanotubes (CNTs), metal oxides, sheet-like zeolites, and graphene oxide (GO), have attracted wide attention. In this paper, GO and single-walled carbon nanotubes (SWCNTs) were selected as the dopants for a Pebax1657 membrane with the goal of surpassing the Robeson upper bound. The Robeson upper bound refers to the balance between permeability and selectivity in most membrane materials [17–19]. Because the internal surface of CNTs is smooth and has large pores, its gas permeability is several orders of magnitude larger than that of other inorganic fillers. At the same time, even at a low concentration in a polymer matrix, CNTs can considerably improve the mechanical strength of the polymer. The key shortcoming of CNTs is their lack of selectivity to different molecules; additionally, the internal channel of a CNT is nonreactive, so it is difficult to add

groups to improve its selectivity [20–22]. This problem can be solved by adding GO as the dopant. GO has a profound effect on gas transport. GO is the oxidation state of graphene, has a large specific surface area, and has good compatibility with polymers, so it can be used as a nanofiller in MMMs [23–26].

In this paper, solution blending was used to form membranes. After the Pebax1657 dispersion, GO dispersion, and SWCNT dispersion were blended, the mixture was dried at 60 °C to obtain the GO/SWCNT/Pebax1657 MMM. Through transmission electron microscopy (TEM), field-emission scanning electron microscopy (SEM), atomic-force microscopy (AFM), X-ray diffraction (XRD) patterns, Fourier transform infrared (FTIR) spectroscopy, and thermogravimetric analysis (TGA), the prepared GO/SWCNT/Pebax1657 MMM was analyzed, and its selectivity and permeability to single gases (CO₂ and N₂) and mixed gas (CO₂ (volume fraction 60%), N₂ (volume fraction 20%), and CO (volume fraction 20%)) at different feed pressures and different temperatures were studied.

2. Experiment Method

2.1. Material and Chemical Reagent

Pebax MH1657 (composed of 60% poly (ethylene oxide) and 40% polyamide 6, with a density of 1.14 g/cm³) was purchased from Arkema Group. SWCNTs (outer diameter 10–20 nm, length 30–100 µm, purity > 98%) were purchased from Shenzhen Nanotech Port Co., Ltd. (Shenzhen, China) Natural flake graphite (12,000 mesh) was purchased from Qingdao Tianshengda Graphite Co., Ltd. (Tsingtao, China) Concentrated sulfuric acid and concentrated nitric acid were purchased from Tianjin Baishi Chemical Industry Co., Ltd. (Tianjin, China) The above reagents were of analytically pure grade and could be used directly.

2.2. GO Preparation

GO was prepared by the improved Hummer's method. First, 2 g of natural flake graphite was weighed and added to 92 mL of concentrated H₂SO₄ with a mass fraction of 98%, and the mixture was stirred evenly in an ice-water bath at 0–5 °C. Then 2 g of NaNO₃ and 12 g of KMnO₄ were added, and the mixture was mechanically stirred for 150 min. After the reaction had ended, the above mixture was placed in a water bath at 35 °C, followed by adding 184 mL of ultrapure water, and the mixture was mechanically stirred for 30 min. The above mixture was placed in a water bath at 95 °C, mechanically stirred for 24 min, and diluted to 560 mL with warm ultrapure water. After the mixture was mechanically stirred for 20 min, 35 ml of 30% (mass fraction) H₂O₂ was added, and the temperature was held for 10 min. Finally, the obtained mixture was left standing for 24 h, and then the supernatant solution was removed. The precipitate was washed repeatedly with 1% HCl until there was no SO₄^{2−} and then washed with distilled water until it was neutral. After freeze-drying, GO was obtained.

2.3. Purified SWCNTs

Two grams of original SWCNT was added into the mixed acid solution, with a volume ratio of concentrated H₂SO₄ to concentrated HNO₃ of 3:1. The mixture was stirred slowly, sonicated for 20 min, and then placed in a water bath at 60 °C. After being stirred mechanically for 180 min, the mixture was diluted to 1200 mL with warm ultrapure water and then allowed to stand at room temperature for 20 h. The supernatant was removed, and the sample was collected by vacuum filtration and then rinsed with absolute ethanol three times. After vacuum drying at 60 °C, the resulting product was the purified CNTs.

2.4. Preparation of MMMs

The MMM was prepared by solution blending. First, 2 g of Pebax1657 was added into a three-neck flask, followed by adding 45 mL of absolute ethanol and 15 mL of distilled water. The sample was dissolved in a reflux setup at 80 °C for 1.5 h to obtain a stable dispersion of Pebax1657 (wt 2%), which was sonicated for 2 h for later use. Next, 0.1 g of GO

was weighed and added to 20 mL of absolute ethanol, and the mixture was magnetically stirred for 1 h and sonicated for 30 min to yield a stable GO dispersion. Finally, 0.1 g of purified SWCNTs was weighed and added to 20 mL of absolute ethanol, and the mixture was magnetically stirred at 40 °C for 1 h and then sonicated for 30 min to obtain a stable SWCNT dispersion. The above GO dispersion was slowly added to the SWCNT dispersion to ensure that the GO dispersion and the SWCNT dispersion were evenly mixed. Then, the GO/SWCNT mixed dispersion was added dropwise to the Pebax1657 dispersion, and the mixture was magnetically stirred for 1 h and sonicated for 4 h to obtain a stable GO/SWCNT/Pebax1657 mixed dispersion, which was dried under vacuum at 60 °C for 24 h to yield GO/SWCNT/Pebax1657 MMMs. In the gas-separation experiment, we set the ratio of Pebax1657:GO:SWCNT is 20:1:1, as shown in Figure 1. After measurement, the film thickness was 0.1 mm.

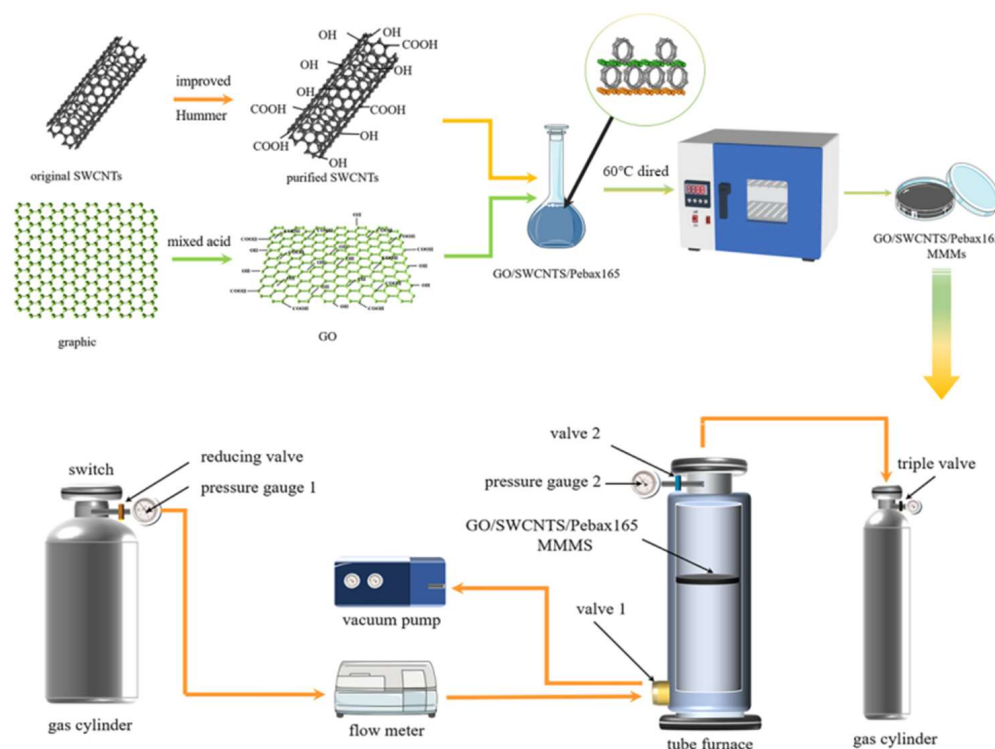


Figure 1. The preparation of MMMs and the performance of gas separation.

2.5. Characterization Methods

SEM (JSM-6700F) was used to analyze the surface morphology of GO and SWCNTs at 5 kV. TEM (type JEM-2010) was used to observe the morphology of the material. An FTIR system (type NICOTCT 5700) was used to analyze the chemical groups on the surface of the material, and the scanning range was 450 to 4000 cm^{-1} . An XRD system (type D8/AXS) was used to determine the crystal structure of the material, with a 2θ range of 5–80° and a step of 4°/min. Differential scanning calorimetry (DSC, type 204HP) and thermogravimetric analysis (TGA, type Q2000) were used to analyze the decomposition behavior of materials at different temperatures. The surface structure and roughness of the Pebax1657 membrane and GO/SWCNT/Pebax1657 MMM were characterized by AFM (type Nano ManVS).

2.6. Gas Permeation Experiment

Using a self-assembled gas-separation experimental device, the pressure difference method was adopted to determine the separation performance of GO/SWCNT/Pebax1657 for single gases (CO_2 and N_2) and mixed gas (CO_2 , N_2 , CO) at different experimental temperatures and feed pressures. The separation equipment is shown in Figure 1. Permeability

and the separation coefficient are important indicators for testing the separation performance of MMMs. The permeability to a single gas was calculated by Equation (1) [27]:

$$P = \frac{QL}{A\Delta p} = \frac{273 \times 10^{10}}{AT[P_0 \times \frac{76}{14.7}]} \frac{dp}{dt} \quad (1)$$

The permeability to each component of the mixed gas was calculated by Equations (2)–(4) [28]:

$$P_{CO_2} = \frac{y_{CO_2}}{\chi_{CO_2}} \frac{273 \times 10^{10}}{760} \frac{VL}{AT[P_0 \times \frac{76}{14.7}]} \frac{dp}{dt} \quad (2)$$

$$P_{N_2} = \frac{y_{N_2}}{\chi_{N_2}} \frac{273 \times 10^{10}}{760} \frac{VL}{AT[P_0 \times \frac{76}{14.7}]} \frac{dp}{dt} \quad (3)$$

$$P_{CO} = \frac{(1 - y_{N_2} - y_{CO_2})}{1 - \chi_{N_2} - \chi_{CO_2}} \frac{273 \times 10^{10}}{760} \frac{VL}{AT[P_0 \times \frac{76}{14.7}]} \frac{dp}{dt} \quad (4)$$

where Q is the volumetric flow rate of permeate gas, cm^3/s ; Δp represents the pressure difference between the two sides of the MMM, mm/Hg ; P represents the permeability, Barrer ($1 \text{ Barrer} = 1 \times 10^{-10} (\text{STP}) \text{ cm} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \text{ cmHg}^{-1}$); V represents the volume of the chamber at the permeate side, cm^3 ; L is the thickness of the MMM, cm ; A represents the effective area of the MMM, cm^2 ; T represents the experimental temperature, K ; P_0 is the initial gas feed pressure, psia ; dp/dt was the rate of pressure increase at permeate side in steady state, cmHg/s ; χ_{N_2} and χ_{CO_2} are the mole fractions of N_2 and CO_2 on the permeate side of the MMM, respectively; y_{N_2} and y_{CO_2} are the mole fractions of N_2 and CO_2 on the feed side of the MMM, respectively; and dp/dt represents the increase in pressure on the permeate side over time.

The ideal gas selectivity is calculated by Equation (5) [29]:

$$\partial_{A/B} = \frac{P_A}{P_B} \quad (5)$$

where P_A and P_B are the permeability of gases A and B , respectively.

The real separation coefficient represents the separation coefficient for mixed gases passing through the membrane and can be calculated by Equation (6) [30]:

$$\partial_R = \frac{y_A/y_B}{\omega_A/\omega_B} \quad (6)$$

where ω_A and ω_B indicate the mole fractions of components A and B on the air inlet side of the membrane, respectively; y_A and y_B separately denote the mole fractions of components A and B on the permeation side of the membrane.

3. Results and Discussion

3.1. Membrane Shape

Figure 2 shows the images of the prepared Pebax1657 and GO/SWCNT/Pebax1657. The pure Pebax1657 membrane was colorless and transparent and had relatively high toughness, fair elasticity, a smooth surface, and good tensile resistance, but the pure Pebax1657 membrane had poor dispersion and easily aggregated, which could lower the gas permeability. Figure 2a,b show the GO/SWCNT/Pebax1657 MMM, which was black and opaque, with poor toughness and brittleness. Both sheet-like GO and CNTs increased the strength of the MMM.

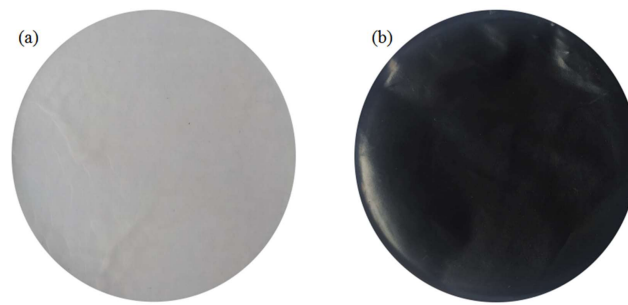


Figure 2. Digital photos of (a) pure Pebax membrane, (b) GO/SWCNTs/Pebax1657 membrane.

3.2. SEM

Figure 3 shows the SEM images of SWCNTs, purified CNTs, GO, and GO/SWCNTs. Figure 3a shows the image of unpurified SWCNTs. They were approximately 3 μm long and had a tube diameter of approximately 8 nm. There were small amounts of impurities and catalysts between the tube walls, the ends were closed, and the aggregation was serious. The image of the SWCNTs purified by mixed acid shows that the aggregation phenomenon was considerably reduced, the CNTs were shortened, the closed ends were opened, and impurities and catalysts disappeared. Figure 3b,c show an SEM image of GO. After repeated ultrasonic exfoliation, there was less accumulation of layer structures, the layer spacing was considerably increased, the overall appearance was an irregular polygonal shape, and the exfoliation effect was good. Figure 3d shows the SEM image of a GO/SWCNT composite. There were lamellar GO and tubular SWCNTs, some CNTs were inserted between the layers of GO, and some were attached to the surface of GO through $\pi - \pi$ bonds. The above demonstrates the successful preparation of the GO/SWCNT composite material.

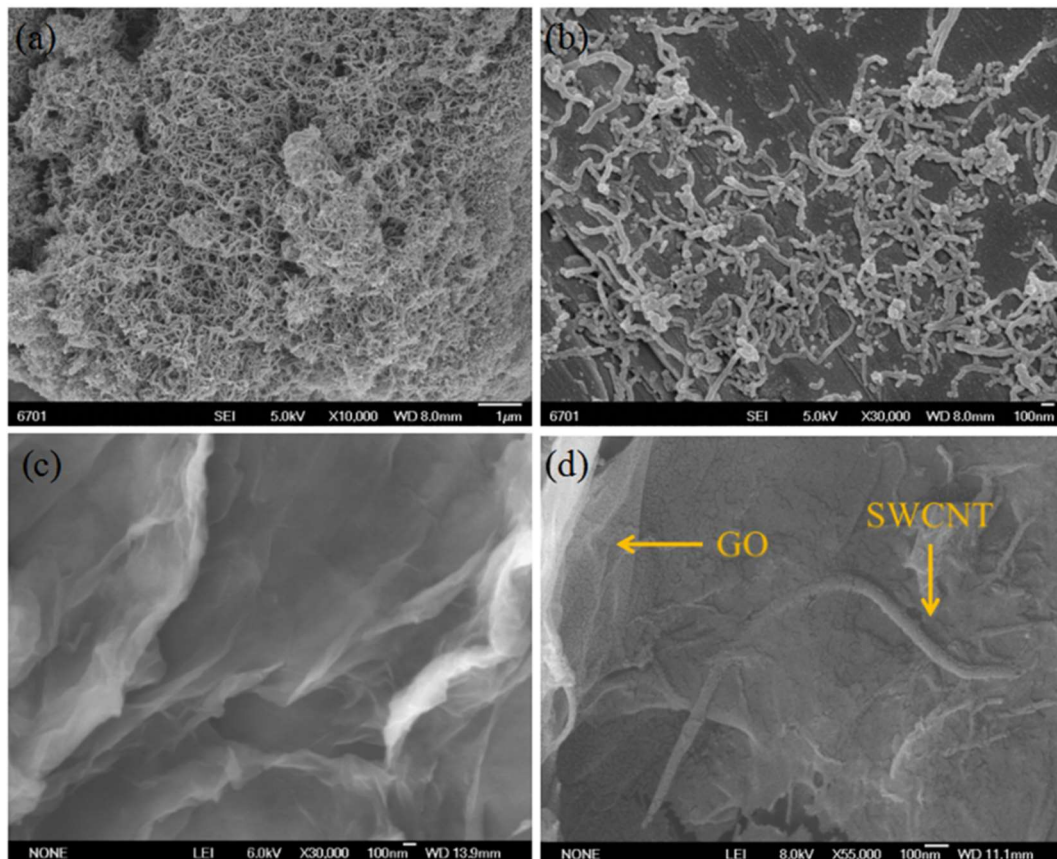


Figure 3. The SEM images of (a) original SWCNTs, (b) purified SWCNTs, (c) GO, (d) GO/SWCNTs.

3.3. TEM

Figure 4 shows the TEM images of SWCNTs, purified CNTs, GO, and GO/SWCNTs. Figure 4a shows that the original CNTs were entangled with each other, they were highly aggregated, the CNTs were irregularly distributed overall, the ends were smooth and closed, and the surface was attached with impurities such as catalysts, so purification treatment was needed. Figure 4b shows the TEM image of SWCNTs purified with mixed acid. The CNTs were shorter, their ends were opened, they had aggregated less, and they were in the shape of a short strip. There was single-layer and multi-layer GO, with wrinkles between layers, which increased the distance among layers. Figure 4c,d show the TEM image of the GO/SWCNT composite. The tubular SWCNTs were attached or embedded in the lamellar GO. The above findings show that the GO/SWCNT was successfully prepared.

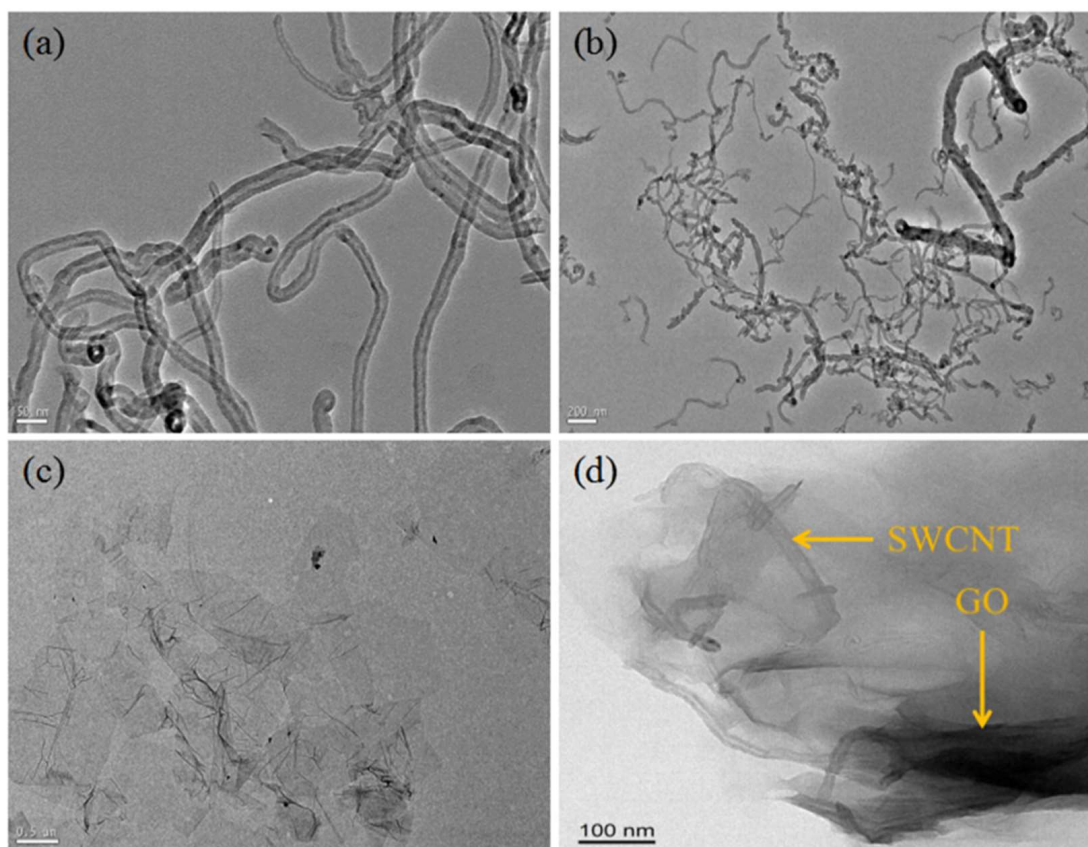


Figure 4. The TEM images of (a) original SWCNTs, (b) purified SWCNTs, (c) GO, (d) GO/SWCNTs.

3.4. FTIR

Figure 5 shows the FTIR spectra of GO, SWCNTs, the Pebax1657 membrane, and the GO/SWCNT/Pebax1657 MMM. The IR spectrum of GO (Figure 5a) showed that the two sharp characteristic peaks at 3436 cm^{-1} and 1400 cm^{-1} were the stretching vibration peak and the deformation peak of -OH, respectively. The characteristic peaks at 1629 cm^{-1} and 1714 cm^{-1} were the C=C stretching vibration peak and C=O stretching vibration peak on the benzene-like ring, respectively. The vibration peak at 1074 cm^{-1} was the vibration adsorption peak of group C-O-C, which originated from the carboxyl, hydroxyl, and epoxy groups of GO. The above results also directly demonstrate the successful preparation of GO [31]. The IR spectrum of SWCNTs showed that the wide and obvious characteristic peak at 3440 cm^{-1} corresponded to the -OH vibration peak [32], which was because large amounts of -OH and -COOH were introduced when CNTs were purified by the mixed acid. The peaks at 2020 cm^{-1} and 1589 cm^{-1} were the C=O vibration peak and C=C vibration peak, respectively; the presence of -CH₃ at 2991 cm^{-1} indicated that the number

of sp^3 -hybridized carbons in SWCNTs and the defects increased after the acid mixing, which indirectly shows that the mixed acid successfully purified the CNTs (Figure 5b).

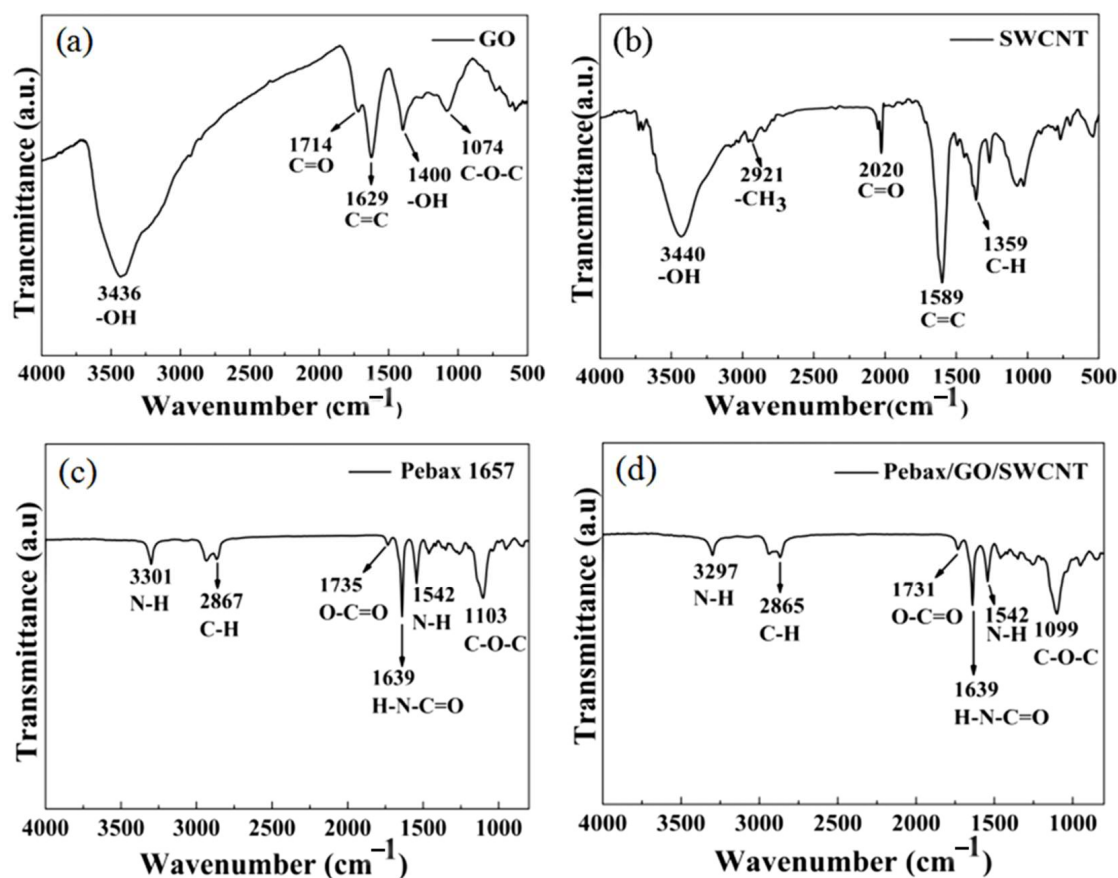


Figure 5. FTIR of (a) GO, (b) SWCNTs, (c) pure Pebax 1657, (d) GO/SWCNTs/Pebax1657.

The IR spectrum of the pure Pebax1657 membrane showed that the characteristic peak at 1103 cm^{-1} belonged to the stretching vibration peak of the flexible segment ether group (C-O-C). The peak at 1639 cm^{-1} was the carbonyl stretching vibration peak of the rigid segment H-N-C=O. The vibration peak at 1735 cm^{-1} was the carbonyl peak of the free group O-C=O [33,34]. The vibration peak at 3293 cm^{-1} reflected the stretching vibration of the N-H group of the amide fragment. The peak at 1542 cm^{-1} originated from the bending vibration of the N-H group. The double peaks near 2867 cm^{-1} corresponded to the asymmetric and symmetric stretching vibrations of the aliphatic chain C-H (Figure 5c) [35]. Figure 5d shows that the IR spectrum of the MMM was almost identical to that of the pure membrane, but the characteristic peaks of GO and SWCNTs were not clearly observed, which may have been due to the relatively low dopant content. Compared with the IR spectrum of pure Pebax1657 membrane, the peak of the carbonyl group of O-C=O at 1735 cm^{-1} , the C-H peak at 2867 cm^{-1} , and the C-O-C peak at 1103 cm^{-1} were all slightly shifted to the right, and the N-H peak at 3293 cm^{-1} was shifted slightly to the left, which was because the addition of GO and SWCNTs destroyed the bonds between the poly(ether-b-amide) molecules and reduced the crystallinity of the membrane. The above results all confirm the successful doping of GO and SWCNTs into Pebax1657. No new peak indicated that Pebax1657 was simply physically blended with the GO and SWCNTs without a chemical reaction occurring. SWCNTs and GO had weak interactions with Pebax molecular chains in the MMM, resulting in the shifts in the characteristic peaks.

3.5. XRD

Figure 6 shows the XRD patterns of GO, SWCNTs, the Pebax1657 membrane, and the GO/SWCNT/Pebax165 MMM. The XRD pattern of GO showed that there was a characteristic diffraction peak of GO at $2\theta = 11.9^\circ$ that corresponded to the (001) crystal plane of GO. The calculated GO spacing was 0.743 nm, indicating that the interlayer spacing of GO was considerably increased compared with the interlayer spacing of natural flake graphite (0.332 nm). This was because large amounts of -COOH and -OH were interspersed in the layers of GO during the preparation of GO, allowing the interlamellar spacing of GO to greatly increase. Figure 6a,b show that two sharp diffraction peaks at $2\theta = 26^\circ$ and 43° corresponded to the (002) and (100) crystal planes of SWCNTs, respectively [36,37]. The XRD pattern of the pure Pebax1657 membrane showed that the original Pebax1657 was a semicrystalline polymer with three characteristic diffraction peaks at 12° , 21° , and 24° . The diffraction peaks at 12° and 21° were the weak peaks formed by the flexible segment of PE, and the characteristic peak at $2\theta = 24^\circ$ was the strong peak due to the semicrystalline structure caused by the hydrogen bond formed between the PA amide groups of the rigid segment (Figure 6c) [38,39]. Figure 6d shows the XRD pattern of GO/SWCNT/Pebax1657. The characteristic peak of GO could be clearly seen near $2\theta = 7.9^\circ$, but compared with the XRD pattern of GO, the characteristic peak of GO in the MMM showed a shift to a low angle (blue shift), indicating that the addition of GO destroyed the molecular force between the polymers, which enhanced the interaction between the polymer and GO and made the molecular chain more dispersed. In addition, a special broad peak near $2\theta = 21^\circ$ was due to the enhancement of Pebax1657, which was because the addition of GO and SWCNTs increased the molecular chain of the MMM, broke the hydrogen bond among the amide groups, reduced the crystallinity, and increased the free volume fraction [40,41]. In addition, there was a sharp characteristic peak near $2\theta = 25^\circ$, suggesting that the SWCNTs were successfully doped into the polymer and that the crystallinity of the nanoparticles was not changed during the membrane preparation process.

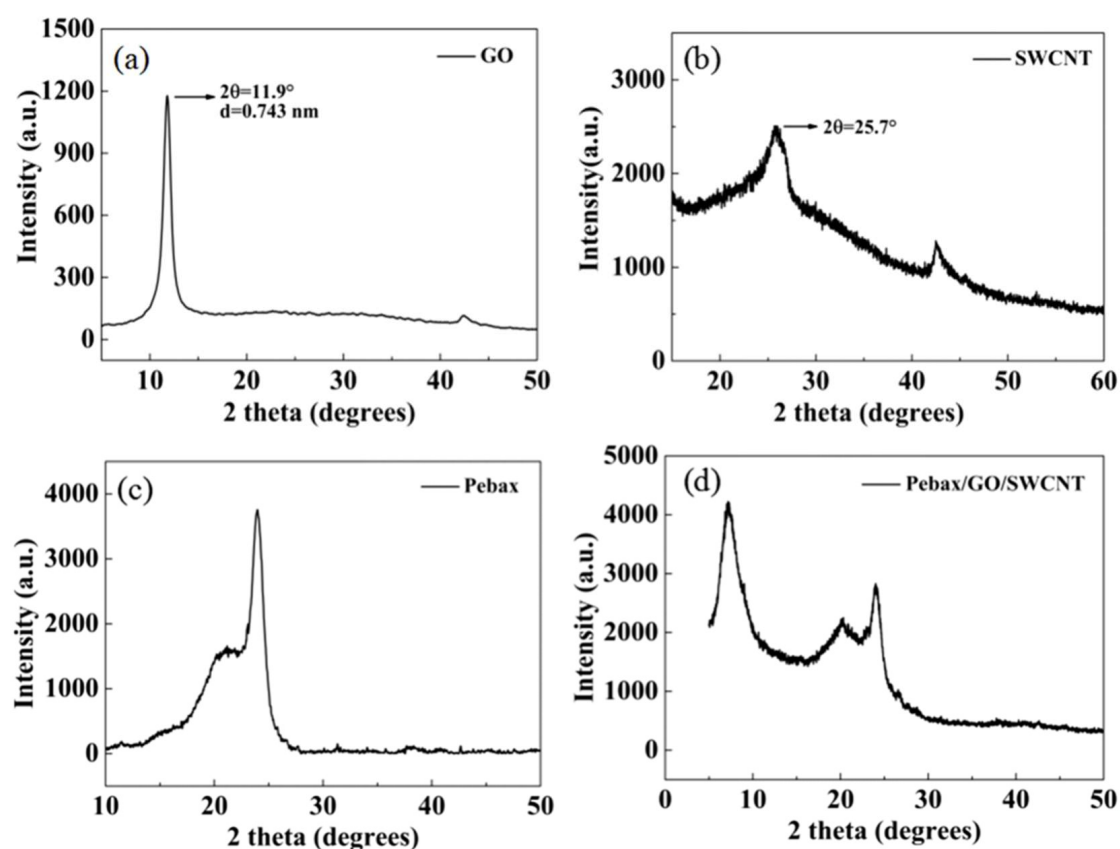


Figure 6. XRD of (a) GO, (b) SWCNTs, (c) pebax1657, (d) GO/SWCNTs/Pebax1657.

3.6. TGA and DSC

Figure 7 shows the TGA and differential scanning calorimetry (DSC) curves of the Pebax1657 and GO/SWCNT/Pebax1657 membranes. Figure 7a shows that the weight loss interval of the Pebax1657 membrane was mostly between 188 °C and 559 °C, mainly due to the thermal decomposition of the poly(ether-b-amide) main chain and the evaporation of water in the membrane [42]. There were two main weight-loss intervals. The first was from 188.5 °C to 445.7 °C, where the weight loss was 79.22 wt%, which was mainly because the poly (ethylene oxide) polyether flexible segment slowly underwent thermal decomposition, and the thermal decomposition rate reached the maximum at 455.7 °C. The second interval was from 445 °C to 559 °C, where the weight loss was 20.78 wt%. The main reason for that weight loss was the thermal decomposition of the rigid segments of PA. The presence of PA segments in the molecular structure was indeed the reason for the good thermal stability of the polymer. The TGA curve of the GO/SWCNT/Pebax1657 MMM showed that there were three main weight-loss intervals. The first stage was from 120 °C to 440 °C, where the weight loss was 77.98 wt%, which had three main causes. The first was the loss of water among the GO sheets and the evaporation of the remaining absolute ethanol in the membrane; the second was the high-temperature thermal decomposition of hydrogen peroxide, sulfate, and nitrate ions that had not been washed away during the preparation of GO and the purification of CNTs; the third was the weight loss caused by the thermal decomposition of the flexible segment in the poly(ether-b-amide) main chain. The second stage was from 440 °C to 490 °C, where the weight loss was 4.57 wt%, mainly due to the decomposition and carbonization of a small amount of MMM and the removal of O and H in the form of small-molecule compounds. The third stage was from 495 °C to 594 °C, where the weight loss was 17.45 wt%, which was mainly due to the thermal decomposition of the rigid segment in the poly(ether-b-amide) molecular chain, the thermal decomposition of a small amount of amorphous carbon in the CNTs, and the thermal decomposition of oxygen-containing groups in GO and CNTs.

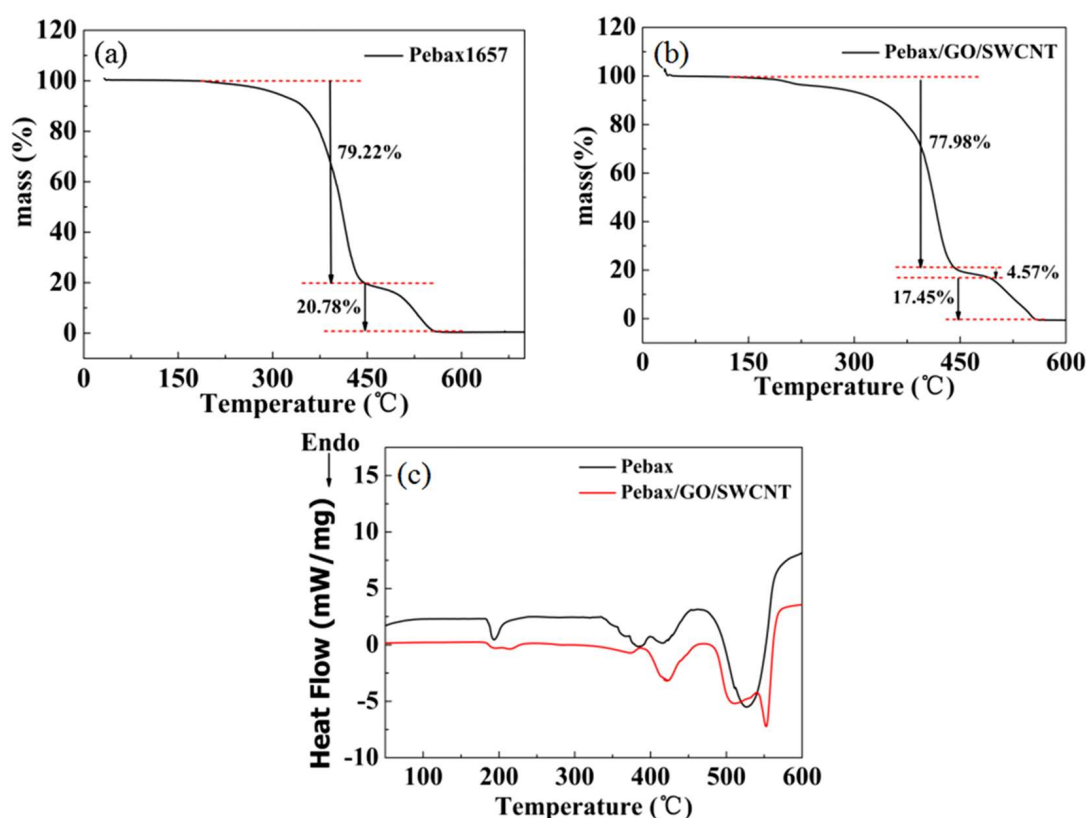


Figure 7. TGA of (a) pure Pebax1657, (b) GO/SWCNTs/Pebax1657 membranes, DSC of (c) pristine Pebax and Pebax/GO/SWCNT.

Figure 7c shows the DSC thermal performance curves of the pure Pebax1657 and GO/SWCNT/Pebax1657 membranes. The pure Pebax1657 membrane had two wide-ranging endothermic peaks at the temperature ranges of 186 °C–206 °C and 486 °C–563 °C, and the amount of absorbed heat at 186 °C–206 °C was 185 J, which was due to the evaporation of water and absolute ethanol. The amount of absorbed heat at 486 °C–563 °C was 3688 J, which was mainly caused by the thermal decomposition of the rigid segment in the Pebax1657 molecular chain. The DSC curve of the GO/SWCNT/Pebax1657 MMM showed that the adsorption peak broadened at 195 °C, which is the glass transition temperature and is usually related to the degree of rigidity of the polymer chain at the filler–polymer interface. In addition, the endothermic peak at a temperature near 426 °C was broadened, and the amount of absorbed heat was 628 J, which was mainly caused by the thermal decomposition of the flexible segment in the poly(ether-b-amide) and the amorphous carbon in the CNTs. The endothermic peak near 560 °C became obviously sharp, the amount of absorbed heat was 2907 J, and the width of the peak narrowed, which was because the membrane may be carbonized at high temperature.

3.7. AFM

AFM is a method of studying the surface roughness of mixed-matrix films. Figure 8a,b show the surface structure of the Pebax1657 membrane and the Pebax1657/SWCNT/GO mixed-matrix membrane. Its scanning range was $3 \times 3 \mu\text{m}$. In Figure 8, bright spots represent humps on the membrane surface, and dark areas represent pits on the membrane surface. There were more ups and downs on the surface of the Pebax film but fewer on the surface of Pebax1657/SWCNT/GO film. After three tests, we calculated that the standard deviations of Ra and Rq of Pebax1657 membrane were 7.09 and 9.39, and the standard deviations of Ra and Rq of GO/SWCNT/Pebax1657 membrane were 0.53 and 0.93, respectively. As can be seen from Table 1, the Ra and Rq of Pebax film are much larger than those of Pebax1657/SWCNT/GO mixed-matrix film. Therefore, the addition of SWCNT and GO reduces the surface roughness of the Pebax film; that is, the surface of the Pebax1657/SWCNT/GO hybrid matrix film is smoother.

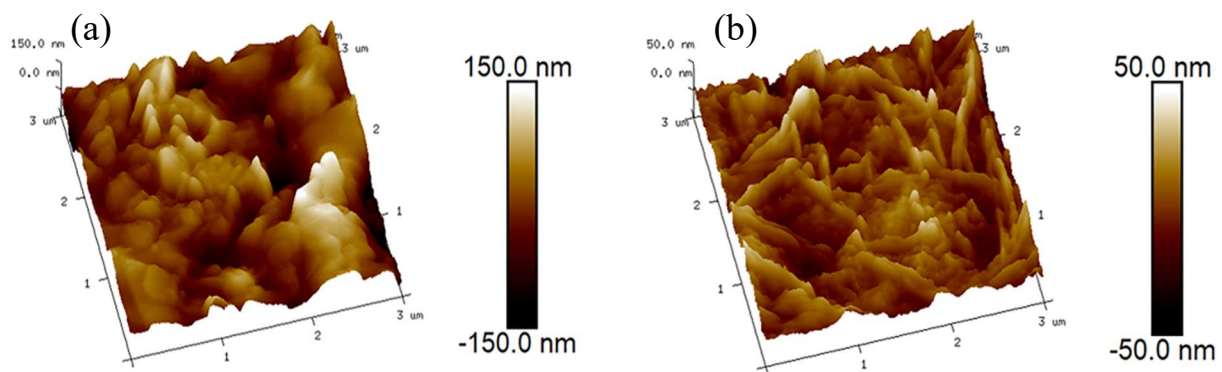


Figure 8. AFM images of the surface (a) pristine Pebax membrane; (b) Pebax/GO/SWCNTs membrane (range of scanning $3 \times 3 \mu\text{m}$).

Table 1. Surface roughness parameters of Pebax1657 membranes and MMMs.

Membranes	Roughness	
	Ra (nm)	Rq (nm)
Pebax1657	24.33	30.83
Pebax1657/SWCNT/GO	7.77	10.22

3.8. Gas-Separation Performance

3.8.1. Single Gas Separation

Figure 9 shows the permeabilities of GO/SWCNT/Pebax1657 for CO₂ and N₂ at different temperatures and pressures. With the increase in temperature, the CO₂ and N₂ permeabilities of GO/SWCNT/Pebax1657 membrane decreased within a certain range. This phenomenon is due to the porosity of SWCNT itself and the gap generated by the interaction between SWCNT and GO, which makes the mixed-matrix membrane have the characteristics of a porous membrane to a certain extent. With increasing feed pressure, the permeabilities to CO₂ and N₂ gradually increased. We conducted a permeability experiment on pristine Pebax1657 membrane and found that under 0.1 Mpa, the permeability of pristine Pebax1657 membrane to CO₂ and N₂ was only 130 Barrer and 40 Barrer, respectively. The pristine Pebax1657 membrane had a permeability of 170 Barrer for CO₂ and 95 Barrer for N₂ at 0.2 Mpa. This is basically consistent with the pristine Pebax1657 membrane permeability reported in the literature [8], so we determined that the effect of the addition of GO and SWCNT was obvious. Since the two are completely not comparable, we only discuss the influence of temperature and air intake pressure on the mixed Pebax1657/SWCNT/GO matrix membrane here.

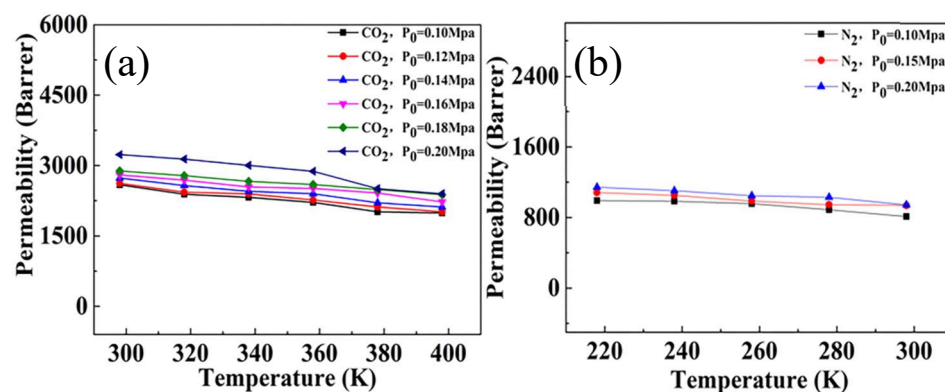


Figure 9. Gas separation performance of GO/SWCNTs/Pebax1657 for (a) CO₂ and (b) N₂ with the increase of temperature and pressure.

At the same temperature and the same feed pressure, the permeability to CO₂ was greater than that to N₂. According to molecular dynamics simulations, the diameters of CO₂, N₂, and CO are 0.33 nm, 0.64 nm, and 0.376 nm, respectively, so the diffusion of N₂ and CO was subjected to greater resistance. The high permeability to CO₂ was also derived from the quadrupole–dipole interaction between the CO₂ and ethylene oxide (EO) units in Pebax, which is supported by the fact that the permeability to CO₂ was higher than that for N₂. With increasing temperature, the permeabilities to CO₂ and N₂ begin to fluctuate, which is because the permeability to CO₂ is caused by its high condensability and the quadrupole–dipole interaction between CO₂ and EO units. When the temperature increases, the CO₂ adsorption of the polymer matrix decreases, so the permeability to CO₂ fluctuates faster than the permeability to N₂. With the increase in temperature, the permeability of the mixed-matrix membrane will fluctuate to a certain extent. At this point, GO begins to play a dominant role in molecular obstruction, and the mixed-matrix membrane doped with GO does not strictly obey the diffusion law of molecular dynamics diameter, so fluctuations occur. Moreover, the collision probability between gas molecules and GO is greater than that between gas molecules, so the permeabilities of CO₂ and N₂ fluctuate.

As the feed pressure increased, the permeabilities to CO₂ and N₂ increased considerably for the following two reasons. Firstly, with the increase in the feed pressure, the driving force of the gas molecules is enhanced, and the permeability is increased. Secondly, due to the increase of the concentration of gas molecules in the polymer, the plasticizing effect is caused. The plasticizing effect increases the mobility of the segment chains and the fractional free volume in the polymer, increasing the permeability of the membrane.

Compared with pristine Pebax1657 membrane, the Pebax1657/SWCNT/GO mixed-matrix membrane has significantly improved permeability to single gas, which we believe is mainly due to the following reasons. First of all, the carbon nanotubes in absolute ethanol cannot completely disperse, so the carbon nanotubes have certain agglomeration, and the agglomeration phenomenon creates a narrow void that facilitates the transportation of gas molecules; furthermore, carbon nanotubes can absorb or contain more gas molecules due to their own defects (heteroatoms, holes, etc.). Secondly, the gas molecules can be rapidly diffused through the carbon nanotubes. Finally, GO and SWCNTs form a wide range of voids to promote the transport of gas molecules, and GO has a large specific surface, which can provide more adsorption sites. For the above reasons, the mixed-matrix membrane of Pebax1657/SWCNT/GO has better osmotic performance than the pristine Pebax1657 membrane.

3.8.2. Mixed-Gases Separation

Figure 10 shows the permeability of GO/SWCNT/Pebax1657 to mixed gas with changes in temperature and pressure. With the increase in temperature, the permeability of CO₂, N₂, and CO fluctuated within a certain range, the permeabilities to CO₂, N₂, and CO gradually increased. This was found to be the same as the permeability relationship of a single gas. However, at the same feed pressure and temperature, the permeabilities of CO₂ and N₂ in the mixture were slightly lower than that of the single gas. This is due to the possibility of the competitive adsorption of gas molecules when mixed gases are separated. We tested the Pebax1657 membrane under the same conditions. At 0.1 Mpa, the permeabilities of CO₂ and N₂ were only 130 Barrer and 40 Barrer, respectively, which were much different from the permeability of the Pebax1657/SWCNT/GO mixed-matrix membrane. Therefore, we believe that SWCNT and GO have obvious effects as dopants for polymer films. SWCNT provides a fast channel for gas molecules. The defect of SWCNT itself enables the mixed-matrix membrane to store more gas molecules. SWCNT and GO are intertwined, and nodules provide more spaces to promote the transport of molecular gases.

Under the same experimental temperature and the same feed pressure, the permeabilities of all components in the mixed gas were in the order of CO₂ > N₂ > CO. The permeability to CO was only in the tens to hundreds of molecules range. The separation of CO₂ was due to the quadrupole–dipole interaction between CO₂ and Pebax and the small molecular diameter. The separation of N₂ and CO was the result of the combined effect of the small molecular diameters and the strong adsorption capacity [43]. When a mixed gas is separated, the separation coefficient is determined by the gas diffusion capacity, competitive adsorption, or both.

3.8.3. Selective Ability for Mixed Gases

The permeability and the separation coefficient of the GO/SWCNT/Pebax1657 MMM during the separation of the mixed gas were next obtained (Figure 11). When the temperature was 298 K and the feed pressure was 0.1 MPa, the permeabilities to all components in the mixed gas were as follows: CO₂ (1806.2 Barrer), N₂ (582.9 Barrer), and CO (136.8 Barrer), and the selectivity was as follows: α (CO₂/CO) = 21.86, α (N₂/CO) = 12.29, and α (CO₂/N₂) = 15.71. When the temperature was 298 K and the feed pressure was 0.15 MPa, the permeabilities to all components in the mixed gas were as follows: CO₂ (1954.7 Barrer), N₂ (630.9 Barrer), and CO (148 Barrer), and the selectivity was as follows: α (CO₂/CO) = 20.44, α (N₂/CO) = 11.27, and α (CO₂/N₂) = 16.03. When the temperature was 298 K and the feed pressure was 0.20 MPa, the permeabilities to all components in the mixed gas were as follows: CO₂ (2439 Barrer), N₂ (787 Barrer), and CO (184 Barrer), and the selectivity was as follows: α (CO₂/CO) = 20.41, α (N₂/CO) = 11.61, and α (CO₂/N₂) = 17.03. The results showed that at the same temperature, with increasing feed pressure, the selectivity for CO₂/N₂ slightly increased, but the selectivity for CO₂/CO and N₂/CO decreased slightly. By comparison with Robeson upper bound, the gas selectivity of Pebax1657/SWCNT/GO mixed matrix membrane (CO₂/N₂, CO₂/CO, N₂/CO)

is higher than that of PEBAx membrane (CO_2/N_2 , CO_2/CO , N_2/CO). In other words, the addition of SWCNT and GO dopants simultaneously improves the permeability and selection performance of the membrane and breaks through the Robeson upper bound to a certain extent.

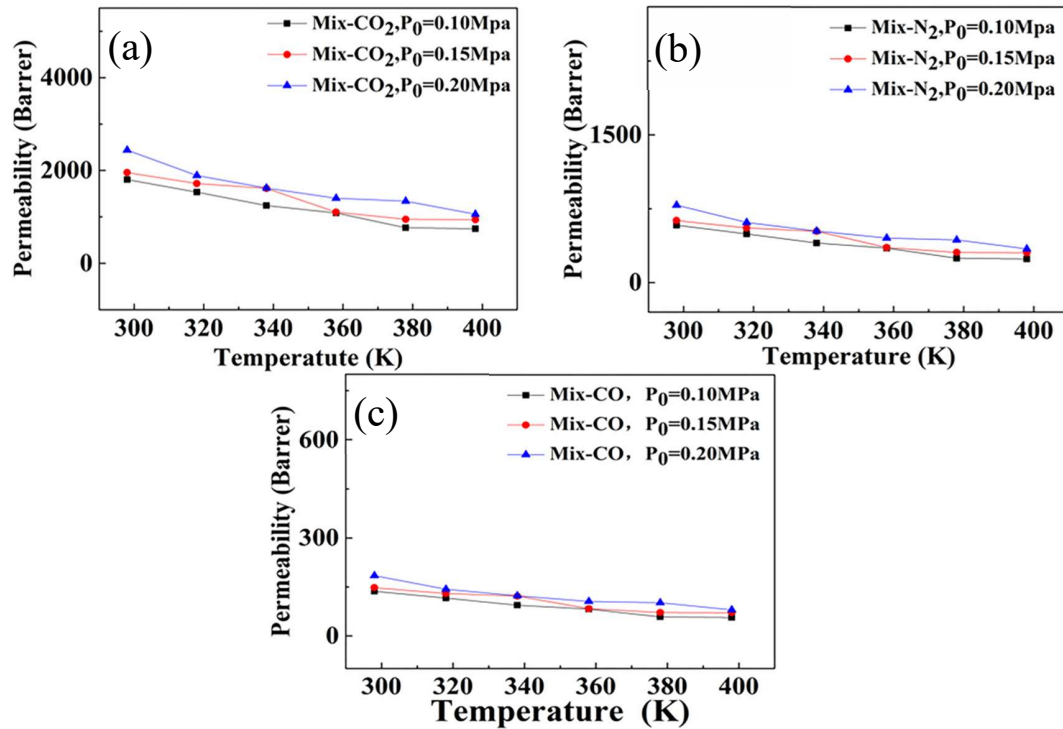


Figure 10. Gas separation performance of Pebax/GO/SWCNTs for mix gas (N_2 60%, CO_2 20%, N_2 20%), (a) CO_2 , (b) N_2 , (c) CO .

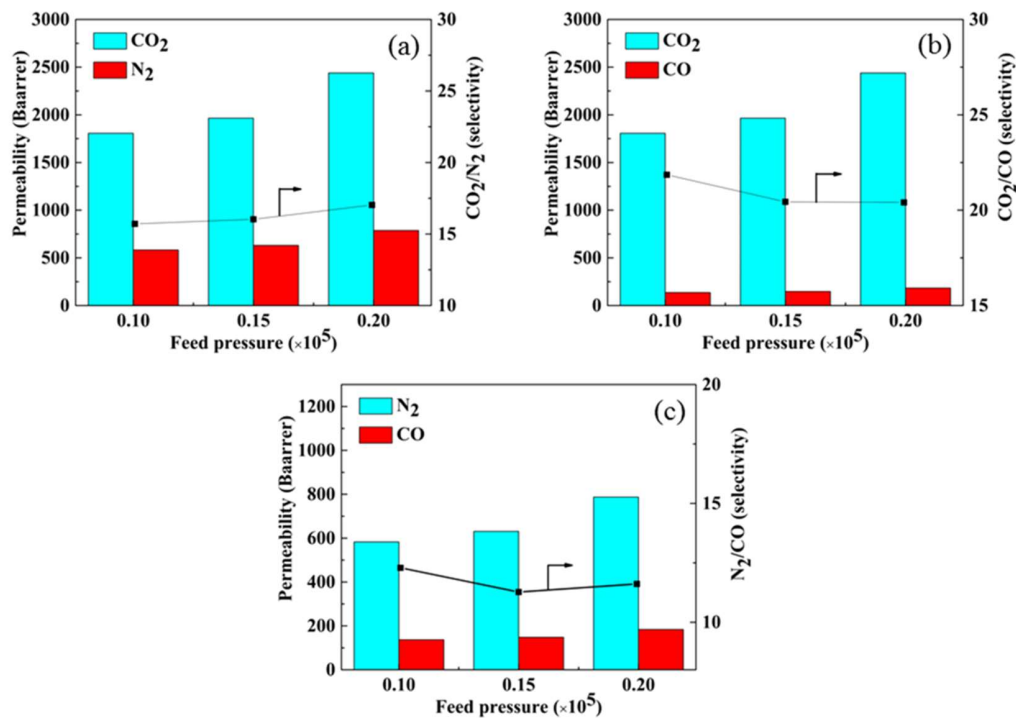


Figure 11. Gas selectivity of Pebax/GO/SWCNTs MMMs for mixed gas (N_2 60%, CO_2 20%, N_2 20%), (a) CO_2/N_2 , (b) CO_2/CO , (c) N_2/CO .

GO/SWCNT/Pebax1657 exhibited high selectivity for gas separation in the mixed gas; as the feed pressure increased, the selectivity for each component in the mixed gas remained basically unchanged, so the increase in feed pressure was only reflected in the increase in permeability and had a minor effect on the separation performance. The differences in selectivity between CO₂, N₂, and CO were due to the different molecular diameters of the three gases, so the differences in selectivity for gas separation may be caused by configurational diffusion. This slight difference could have underlain the significant changes in the diffusion coefficient of the pore channel in the MMMs, resulting in the separation differences and thus relatively high separation selectivity. The GO/SWCNT/Pebax1657 MMM possessed regular nanochannels. The results showed that the GO/SWCNT/Pebax1657 MMM can separate N₂ and CO₂ from the mixed gas, and the separation performance for CO₂/CO was the best, followed by N₂/CO. The GO/SWCNT/Pebax1657 MMM could separate the inert gases N₂ and CO₂ from the blast furnace gas, thereby increasing the calorific value of CO, giving this membrane theoretical significance for the study of the secondary utilization of blast furnace gas.

4. Conclusions

In this paper, GO was prepared by the improved Hummer's method, and a GO/SWCNT/Pebax1657 MMM was prepared by solution casting. SEM and TEM images showed that the lamellar GO and the tubular CNTs were intertwined, and the GO and SWCNTs to the Pebax matrix were added by simple physical mixing. AFM images showed that the addition of GO and SWCNTs could disrupt the accumulation of polymer matrix molecular chains, increase the surface roughness of the membrane, and reduce the crystallinity of the membrane. Gas-separation experiments showed that when the temperature was 298 K and the feed pressure was 0.2 MPa, the permeability of GO/SWCNT/Pebax1657 for CO₂ reached 3233 Barrer, and the permeability to N₂ reached 1153 Barrer. When the feed pressure was 0.2 MPa and the temperature was 298 K, the permeabilities of GO/SWCNT/Pebax1657 for CO₂, N₂, and CO in the mixed gas reached 2439 Barrer, 787 Barrer, and 184 Barrer, respectively. The selectivity of GO/SWCNT/Pebax1657 was in the order of $\alpha(\text{CO}_2/\text{CO}) > \alpha(\text{CO}_2/\text{N}_2) > \alpha(\text{N}_2/\text{CO})$, which fully demonstrates that the GO/SWCNT/Pebax1657 MMM can effectively separate CO₂ and N₂ from blast furnace gas. This MMM has excellent gas permeability and selectivity and provides a new way to separate CO₂ and N₂ from blast furnace gas.

Author Contributions: L.L.J.: Methodology, Investigation, Funding acquisition. Y.X.C.: Writing review & editing, Writing original draft. X.G.H.: Software, Validation. All authors have read and agreed to the published version of the manuscript.

Funding: The authors are grateful for the financial support from the National Natural Science Foundation of China (52064036, 51764039), Talents innovation and entrepreneurship project of Lanzhou (2021-RC-36), Outstanding Youth Fund of Gansu Province (22JR5RA220), Basic Public Welfare Research Project of Zhejiang Province (LQ19E040006) and State key laboratory of advanced processing and recycling of non-ferrous metals, Lanzhou University of Technology (SKLAB02019013).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: All data generated or analyzed during this study are included in this article.

Conflicts of 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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