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Fabrication and characterization of polysulfone-graphene oxide mixed matrix membranes for the effect of glass transition temperature of polymer on the selective layer for separation

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Abstract

The polysulfone mixed matrix membranes (MMM) with concentrations of graphene oxide (0.0, 0.25 and 0.5 wt.% of polymer) fabricated by a phase separation method.the obtained results show that the kinetic selectivity means the ratio of the penetration coefficients of two gases, which expresses the different sizes of the two gases CO_2/N_2 and CO_2/CH_4. first, by adding 0.25 percent by weight of graphene oxide to the composite matrix, the selectivity of CO_2/N_2 became 12.24 and 50 percent by weight of graphene oxide was 17.79. while CO_2/CH_4 selectivity was 10.94 and 14.14 respectively. For this purpose, by addition of graphene oxide to the membrane structure, Tg increased considerably due to the strong bond between polysulfone and graphene oxide. These strong bonds are due to the active agent groups present in the surface of graphene oxide, which have established a good bond with the polymer.

Keywords: Membrane gas separation, Mixed matrix membrane, Graphene oxide

1. Introduction

Inorganic membranes are able to withstand high temperature and are durable compared to the polymer membranes. Researchers seek to find methods to achieve the benefits of both polymeric and inorganic membranes in a simultaneous manner.To fabricate MMMs, inorganic fillers are applied in the polymer membrane matrix. In recent years, MMMs have been used for different applications like gas separation, water desalinization, heavy metals removal from water, gas absorption and discharges.

Graphene, known as low permeability filler, has not been for gas separation in fabrication of MMMs considered. Natural graphene is an inert substance and its ability to propagate in the solvents and the reaction is very low, therefore it does not form a homogeneous mixture with the polymer. In order to increase the stability of graphene in solvents and form a bond with the polymer chain, introducing groups functional on the graphene surface is essential. it is a graphene-based nanoparticle, and is linked to oxygen-bound groups. Active cell groups, like carboxyl and hydroxyl in graphene oxide, can propagate in the polymer matrix in a proper manner which can improve the membrane gas separation properties [1, 2]. Applying graphene oxide for MMM fabrication forms a pathway for small gas molecules passages and prevents the large gas molecules' passage [3, 4]. Recent studies have shown that presence of graphene oxide nanoparticles in the membrane structure increased the mechanical and thermal stability of the membranes [5-9]. Researchers have found that by adding graphene oxide to the polysulfone hollow fiber membrane structure, tensile strength and length stretching increased during membrane breakage by 36.3% and 8.79%, respectively [10]. It is also observed that the graphene polysulfur-oxide mixed matrix membrane has a high thermal stability and its mechanical properties increased when 0.25% graphene oxide was added to the matrix [11].

According to the latest studies, graphene oxide is rarely applied in improving the structure of polymeric membranes for nitrogen/carbon dioxide/methane separation. In this study, polysulfone MMMs were prepared by applying graphene oxide as a filler additive. After assessing the structure and specifications of the membranes, they were applied in nitrogen/carbon dioxide/methane gas separation.

2. Experiments

2.1 Materials

Polysulfone (PSd Udel P-3500, Amoco Chemicals, USA) was applied as the base polymer for membrane fabrication. The reason for selecting this polymer is its good mechanical stability and ease of processing[12-15]. N-methyl-acetamide solvents of (DMAC> 95%) and tetrahydrofuran (THF≥ 99%) were purchased from the Merck, and used as the solvents. Natural graphene sheets (≤ 23μm), ethanol and potassium permanganate (KMnO4) were purchased from Sigma Aldrich. Concentrated sulfuric acid (H_2SO_4, 90-95 wt. %), hydrochloric acid (HCl) and hydrogen peroxide solution (H_2O_2, 29 wt. %) were provided from Merck, Germany. distilled water was produced in the laboratory and used as the coagulant in the process of fabricating membranes.

2.2 Preparing the polymer solutions

In order to fabricate the MMMs, three types of the polymer solutions were prepared as follows:

The first solution was free of graphene oxide, where the solution contains polysulfone polymer (30 wt.%), dimethyl acetamide (35 wt.%), tetrahydrofuran (30 wt.%) and ethanol (5 wt.%). The ratios representing the polymer solutions are given elsewhere[12,17,18]. To prepare 100g of this solution, first, 35g of DMAc solution was poured into a glass bottle and then 30g of tetrahydrofuran was added. When the mixture of solvents in the bottle was stirred by a mechanical stirrer, 30g of polymer was gradually added to the solvent. The gradual addition of the polymer prevents agglomeration of the polymer seeds. The solution was stirred for 24 hours to dissolve all the polymer in the solvent. After making sure that all polymer seeds in the solvent were dissolved, 5g ethanol was added to the solution and the solution was stirred again for 2 hours to achieve a homogeneous solution. To remove the air bubbles in the solution, the solution bottle was placed in ultrasonic apparatus for 1 hour and then kept at ambient temperature for 24 hours. The method of making other two solutions is according to the method of making the first solution. with the difference that the concentration of graphene oxide used in the second and third solution is 0.25 and 0.5 (weight percent), respectively.

2.3 Characterization of the fabricated membranes

2.3.1 Scanning electron microscopy (SEM)

To display cross-sectional and surfaces images of the fabricated membranes, scanning electron microscopy (TM3000, HITACHI, Japan) was used. Small pieces of 5×5 cm membranes were cut in liquid nitrogen, so that the cross-sectional structure would break with no failure. The broken parts are placed in an oven at 60 °C for 2 hours for moisture removal in the pores of the membranes.

2.3.2 Atomic force microscopy (AFM)

To assess the membrane surface roughness and determine the average roughness (Ra), atomic force microscopy (AFM, SPA-300 HV, Seiko, Japan) was applied. For this purpose, small pieces of 5×5 cm membranes were cut and the surface roughness was assessed by AFM.

2.3.3 Mechanical stability of the membranes

Tensile strength and elongation at the breaking point of the fabricated membranes were measured according to ASTM D3039 through a tensile test machine (LRX 2.5 SKN Llyod). For this purpose, the membranes were cut to pieces of 5 cm in length and placed in the device. At least five samples for each membrane were tested and the average value was reported.

2.3.4 Differential scanning calorimeter

To determine the glass transition temperature (Tg) of the prepared membranes, a differential scanning calorimeter model (DSC, Mettler Toledo DSC, 822e) was applied. The membrane samples were heated from 30 °C to 400 °C at an intensity of 10 °C / min, after

which the cooling took place in the reverse manner. The hot and cold operation was run twice: the first was to calibrate the sample and the second was to determine Tg.

2.3.5 Thermal gravimetric analysis (TGA)

Thermal stability analysis of graphene oxide and the prepared membranes were conducted through a thermal gravimetric analyzer (TGA, Perkin Elmer). The sample was heated until a change in weight was observed. The sample was heated within 30 °C to 805 °C at 10 °C / min intensity in a nitrogen atmosphere at 22 ml/ min flow rate.

2.3.6 Membrane gas separation test

The final function of the membrane is affected by the following structural changes:

Level 1: Chemical decomposition of the polymer that forms the retaining and selector layer of the membrane, polymer chemistry It affects the penetration rate of gas molecules through the membrane.

Level 2: Repeated spatial relationships in the structure of the surface-selective polymer (polymer chemistry and its effect on the penetration rate) gas molecules from the membrane).

Level 3: The surface membrane separator layer (membranes divide gas separation into symmetric and asymmetric do).

Level 4: The overall structure of the membrane requires a structural relationship between the retaining layer and the separating layer. (it is the local structure of the membrane or the membrane process system, and it means all the properties and hard

The required software is suitable for a gas separation module.

According to the following performance equation:

$$\mathbf{J_i=(D_iK_i^G(p_{io}-p_{il}))/L}$$

Where J_i is the flux of the i component and P_{io} and P_{il} are the partial pressure of the i component on both sides of the membrane, L is the membrane thickness, DI Penetration force and K^G is the absorption force of the art law.

Determining the ability of the membrane to separate two types of gas i and j can be done as a ratio the permeability of these two gases was defined, and this ratio is called membrane selectivity and is expressed by the following relationship made:

$$\mathbf{\alpha_{ij}=(D_i/D_j)*(k_i/k_j)}$$

The D_i/D_j ratio is the ratio of the penetration coefficients of two gases and can be called kinetic selectivity. which expresses the different sizes of two gases, the K_i/K_j ratio is the ratio of the absorption coefficients of the two gases and it can be called adsorption selectivity, which expresses the relative condensability of two gases. So

Membrane selectivity is a function of two factors, kinetic selectivity and adsorption selectivity.

In the gas separation process, the selectivity of the membrane strongly depends on whether the membrane-forming polymer is high or low temperature it depends on the glass transfer.

3. Results and Discussion

3.1 Structural morphology of the prepared membranes

The scanning electron microscopy was used to evaluate the cross-sectional structure of the membranes and the images are shown in Fig. (1).

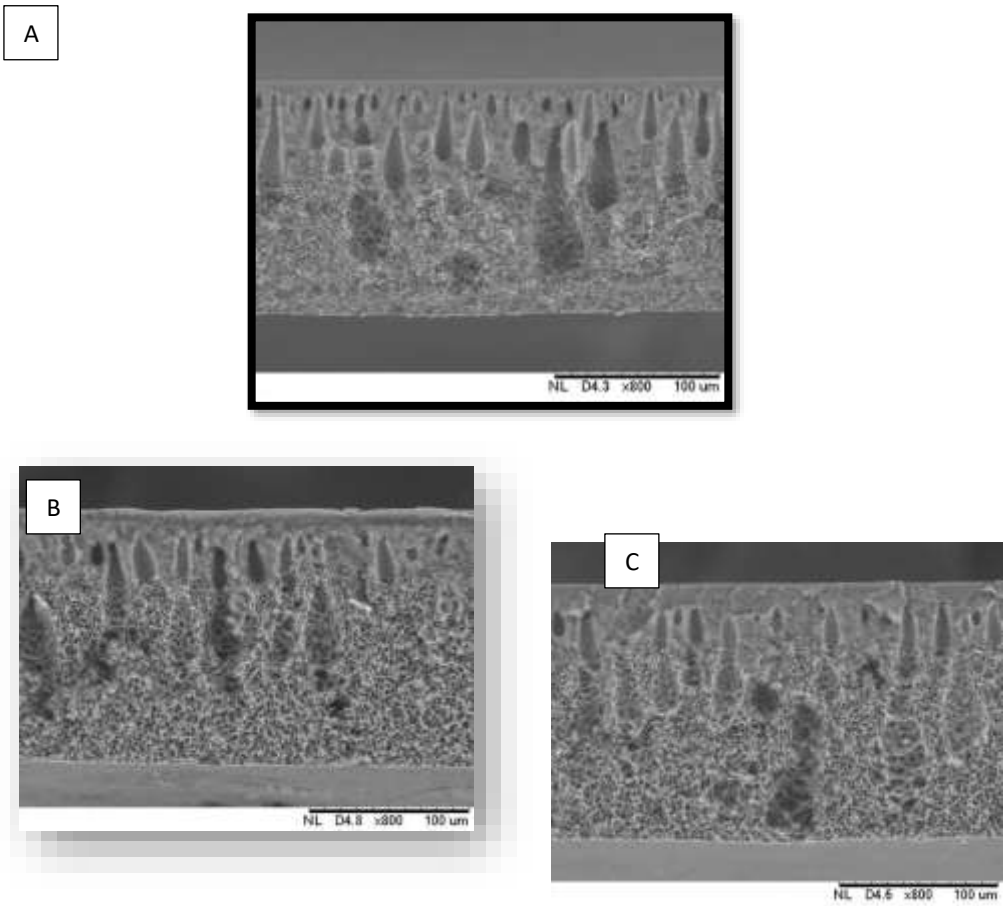

Figure 1: SEM cross-sectional images of the prepared membranes

(A) Pure polysulfone; (B) 0.25 wt. % GO; and (C) 0.50 wt. % GO

From cross-sectional images, the fabricated membranes showed an asymmetric structure, which consists of a dense active skin with a thin sponge-like substrate and a thick fuzzy layer with large cavities. Using 2 min. air gap time before immersion of the membrane in the coagulation bath, evaporation of THF resulted in formation of a thin selective layer on the top surface of the membrane[17]. Moreover, formation of spongy and finger-like structure during the wet phase separation process can be related to the exchange of solvents (DMAc, THF and EtOH) and non-solvent (water) contained in the coagulation bath. In general, when the rate of the phase separation process and the solvent/non-solvent

exchange are high, a finger-like structure is formed, while the formation of sponge-like structure is related to a low rate of phase separation[26]. The formation of a finger-like or sponge-like structure in phase separation process depends on the viscosity and thermodynamic instability of the polymer solution, where an increase in the viscosity of the polymer solution decreases the rate of phase separation process, thus resulted in a sponge-like structure.

3.2 TGA and DSC analysis of the prepared membranes

The glass transition temperature (Tg) of the fabricated membranes was determined through differential scanning calorimetry analyzer (DSC). The interactions between graphene oxide and polysulfone can be predicted by applying the Tg values. The results of Tg and the decomposition temperature of the fabricated membranes are shown in Table 1.

Table 1: T g and decomposition temperature of the fabricated membranes

Membrane name	T_g °c	T_d °c
M_1	190	500
M_2	214	515
M_3	217	540

As observed in Table1, by addition of graphene oxide to the membrane structure, Tg increased considerably due to the strong bond between polysulfone and graphene oxide. These strong bonds are due to the active agent groups present in the surface of graphene oxide, which have established a good bond with the polymer[3]. These links prevent the mobility of polymer chains and increased the Tg value. In another study, a reduction in Tg was observed by adding halothon nanotubes (HNT) to the polymer matrix[30]. This reduction could be related to a poor adhesion between the filler and the polymer matrix, which lead to the formation of cavities around the filler surface.

3.2.1 DS : Differential scanning calorimeter

In this method, a small sample of polymer is prepared and given heat, and during this time, the amount of energy required to give heat to the sample is measured. Since the physical properties change in the glass transition range, the energy required to heat the sample also changes. This is shown as a bend in the diagram. The following figure shows the glass transition temperature analysis.

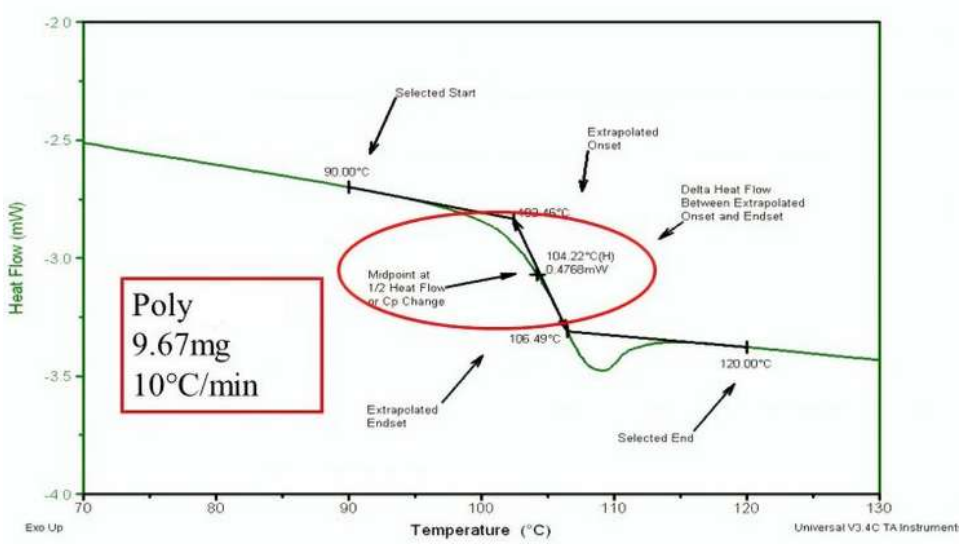

Figure 2 :Determination of glass transition temperature by method

3.4 Gas separation performance of the prepared MMMs

Selectivity of the prepared membranes is shown in Fig. 3.

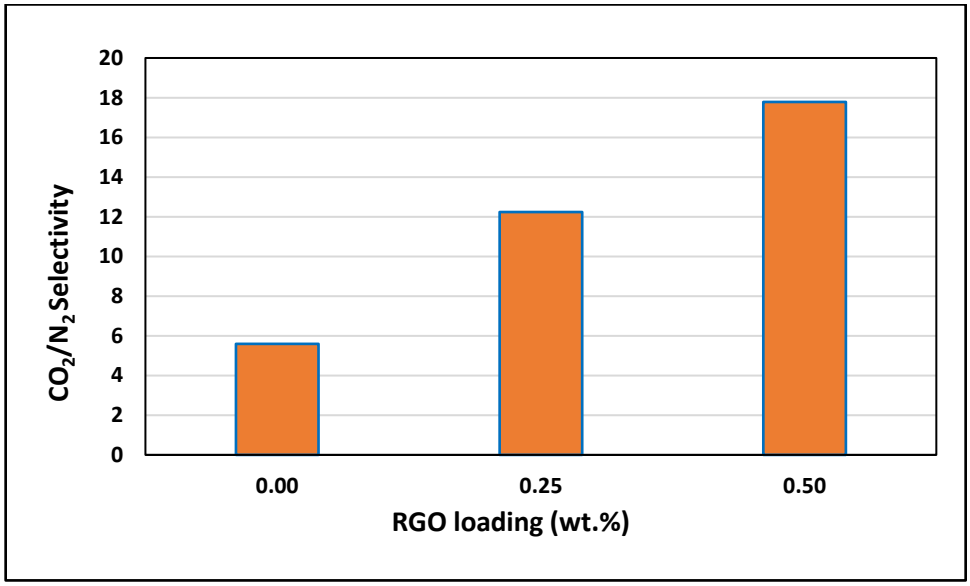

Figure 3: Carbon dioxide selectivity in relation to nitrogen and methane

An increase in the graphene oxide concentration increased CO_2 selectivity of the membranes. In the explanation of the results of the membrane surface images it was explained that by adding graphene oxide to the polymer solution, a thin layer of integrated monolithic was formed. The inert gas molecules like nitrogen did not pass, thus resulted in improvement of the membrane selectivity.Therefore, for M1, M2 and M3 membranes, carbon dioxide selectivity for nitrogen is 5.60, 12.24 and 17.79, respectively. Carbon dioxide selectivity for methane was 5.41, 10.94 and 14.14, respectively.

Selectivity of the prepared membranes is shown in the following table2

Table 2: Selectivity of the prepared membranes

	M_1	M_2	M_3
CO_2/N_2	5.6	12.3	17.8
CO_2/CH_4	5.4	11	14.2

Table 3: Comparison of the Selectivity different membranes

Membrane	Polymer	Filler	Selectivity CO_2/N_2	Reference
Flat sheet [a]	Polysulfide	FCF (nano)	2	28
Flat sheet [b]	Polysulfide	CNF	10	31
Flat sheet [c]	Polysulfide	C15A2.0%wt	4	11
Flat sheet [c]	Polysulfide	GO(0.25wt%)	12	This study

a $_p$=2 bar at ambient temperature

b $_p$= 4.48 bar feed pressure at ambient temperature

c $_p$=6 bar feed pressure and T= 28 ^{o} C

As observed of table 3, the membrane fabricated with 0.25% of graphene oxide exhibited a better performance for the separation of carbon dioxide and nitrogen.

4. Conclusion

by addition of graphene oxide to the membrane structure, Tg increased considerably due to the strong bond between polysulfone and graphene oxide. These strong bonds are due to the active agent groups present in the surface of graphene oxide, which have established a good bond with the polymer[3]. These links prevent the mobility of polymer chains and increased the Tg value. In another study, a reduction in Tg was observed by adding halothon nanotubes (HNT) to the polymer matrix[30]. This reduction could be related to a poor adhesion between the filler and the polymer matrix, which lead to the formation of cavities around the filler surface.

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